Propagation Rate Coefficient of Vinyl *neo*-Decanoate by Pulsed Laser Polymerization

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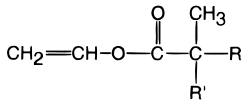
ABSTRACT: The propagation rate coefficient (k_p) for vinyl *neo*-decanoate has been measured by pulsed laser polymerization (PLP) over the range −21 to +21 °C. The Mark−Houwink−Sakaruda constants required for GPC analysis were obtained using size-exclusion chromatography with an on-line viscosity detector, whose analysis required careful quantification of the uncertainties. The data, which satisfy various consistency tests for PLP (invariance of k_p to laser pulse frequency, etc.), fit the relation k_p (dm^3 mol^{-1} s^{-1}) = $10^{7.31}$ exp(−22.2 kJ mol^{-1}/RT); the joint confidence region for these Arrhenius parameters is also given. These Arrhenius parameters are close to those for vinyl acetate [$10^{7.16}$ exp(−20.7 kJ mol^{-1}/RT)]; the small differences between these Arrhenius parameters are, however, statistically significant at the 95% confidence limit. The vinyl *neo*-decanoate used is actually a mixture of isomers: CH_2═$CHOCOCR_1R_2CH_3$, where the total number of carbons in R_1 and R_2 is 7; however, theory suggests that the k_p values for all these isomers should be very similar and polymerization of the mixture can be treated as a homopolymerization with a k_p equal to the average k_p.

Introduction

Vinyl esters of tertiary carboxylic acids are a group of monomers which have been used in the production of latex for water-based paints for some 20 years. In particular, vinyl *neo*-decanoate (V*neo*D) **(1)** is commonly



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copolymerized with vinyl acetate to give a copolymer that has a greater resistance to water and alkaline hydrolysis than a vinyl acetate homopolymer. The commercial monomer is a mixture of isomers, where the total number of carbons in R and R′ is 7. Even though it is widely used in industry, very little information about the fundamental kinetics of free-radical emulsion polymerization of the monomer has been reported in the literature. The existing data comprise monomer reactivity ratios with vinyl acetate and some other monomers determined by a manufacturer.[1]

There is an increasing body of knowledge on the detailed mechanisms on the formation and growth of latex particles; such a mechanistic understanding is useful for the control and improvement of polymer manufacture and properties. In order to elucidate mechanisms for emulsion polymerization from experiment, an important quantity that is required is an accurate value of the propagation rate coefficient, k_p.[2] Knowledge of k_p enables one to go from the observed polymerization rate to the average number of radicals per particle, the latter being a fundamental observable in particle growth mechanisms.

In the present paper, k_p for V*neo*D was determined using the method of pulsed laser polymerization (PLP).[3] This method is recommended by the IUPAC working party on "Modeling of Kinetics and Processes of Polymerization" as the most reliable of the various techniques available.[4−7] Briefly, the method involves the illumination of a mixture of monomer and a photoinitiator with brief light pulses, usually from a laser. Free-radical polymerization of the monomer is initiated by the radicals produced during illumination of the mixture. The radical polymer chains propagate until growth is stopped by bimolecular termination or other chain-stopping reactions, such as transfer. As the rate of bimolecular termination is proportional to the square of the radical concentration, a large number of radical polymer chains terminate during or shortly after illumination. Under favorable conditions a significant number of polymer chains which were initiated during one pulse will terminate with a short radical produced during the subsequent pulse. The degree of polymerization of these polymer chains will be a value L_0 given by

$$L_0 = k_p[\mathrm{M}]t \qquad (1)$$

where [M] is the monomer concentration and t is the "dark" time between pulses.

Modeling of molecular weight distributions under various conditions has shown[8−15] that L_0 will correspond to some value between the point of inflection on the low molecular weight side of the peak molecular weight and the degree of polymerization at the peak. These models show that except for extremely high radical fluxes, the degree of polymerization at the point of inflection is closer to the value of L_0 than the degree of polymeri-

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zation at the peak. As such, a high radical flux is not obtained under the reaction conditions in this work, the degree of polymerization at the point of inflection was chosen as the best estimate of L_0 in determining k_p, this choice being validated by the invariance of the k_p obtained from this inflection point to the pulse frequency and by the appearance of higher overtones at an appropriate multiple of the first point of inflection.

Experimental Section

Pulsed Laser Initiated Polymerization. V*neo*D (Shell Chemicals) was supplied as a mixture of isomers. As shown later, it can be safely assumed that the k_p's of individual isomers will not vary significantly. Thus, while the system is strictly speaking a *co*polymerization, and the value obtained here for the propagation rate coefficient at a given temperature is therefore an *average* (in the Mayo−Lewis sense) over k_p^{ij}'s, it is expected that all of these k_p^{ij} are very close to this average value, which, moreover, is not expected to show any dependence on concentrations of the different isomers. All experiments were conducted with the unresolved monomer mixture to obtain an average k_p. The monomer was washed with 5% NaOH solution, dried over $CaCl_2$, and then distilled under reduced pressure (100 °C, 5 mmHg) prior to use. The photoinitiators used were benzoin (Aldrich) and 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651, Mercury Enterprises), which were used as received. Di-*tert*-butylphenol was used as received to inhibit further polymerization after pulsing.

Gas chromatography analysis of vinyl *neo*-decanoate was carried out using a Hewlett Packard 5890 gas chromatograph, with an HP-FFAP column (10 m × 0.53 mm × 1.0 μm) and a flame ionization detector. High-purity helium was used as the mobile phase.

Cylindrical silica cells (10 mm diameter) were filled with solutions of the photoinitiator in V*neo*D (1 mL). Cells were sealed with rubber septa and purged with nitrogen gas for 2 min. Care was taken to avoid illumination of the solutions during preparation.

Pulsed laser polymerizations of the samples were performed using an XeCl excimer laser of wavelength 308 nm (Lextra 200, Lambda Physik). Approximately 10% of the total pulse energy was incident through the sample from the base of the cell. Pulses were of approximately 10 ns length and at a repetition frequency of either 20 or 30 Hz. Above −8 °C, samples were maintained at the required temperatures by recirculating a glycol/water mixture from an isothermal bath, through a brass cell holder in contact with the sides of the cell. For temperatures below −8 °C, an insulated metal vessel incorporating a cell holder was filled with an ethanol/water/dry ice "slush bath" mixture to obtain the required temperature. Samples were illuminated with either 500 or 1000 pulses depending on the temperature and initiator concentration, in order to keep the conversion of polymer less than 2%. After polymerization, di-*tert*-butylphenol in tetrahydrofuran (0.1 mL, ∼10% v/v) was added to the samples to inhibit further polymerization. The temperature of each sample was measured immediately after the addition of inhibitor with a platinum resistance temperature probe. An increase in temperature due to the exothermic reaction was not detected (the response time of the probe was *ca*. 30 s). The observation that the apparent value of k_p was independent of the time of irradiation suggests that exotherms are not a problem. The slush bath temperature was also monitored to ensure the bath temperature had remained constant during pulsing.

Density of Vinyl *neo*-Decanoate. Density of the monomer was determined at various temperatures relative to water and ethanol using a glass pycnometer (∼50 mL); the monomer density was found to obey d_m (g cm^{-3}) = $(1.6264-4.3) \times 10^{-3}T + 5.923 \times 10^{-6}T^2$ (where T is the temperature in K).

Determination of Molecular Weight Distributions. Molecular weight distributions of polymer from PLP experiments were obtained using gel permeation chromatography. Three GPC columns (Waters 10^2, 10^3, and 10^4 Å Ultrastyragel) were used in series with a differential refractive index detector (Waters 401). HPLC grade tetrahydrofuran was used as eluent, pumped at a constant flow of 0.6 mL min^{-1}. Analysis of samples was carried out at room temperature (22 °C). Samples were either injected directly or dried under reduced pressure to measure conversion and then redissolved in tetrahydrofuran (4 mg/mL) prior to injection (50 μL). Conversions of the remaining samples were estimated from the cumulative detector signal relative to samples of known concentration. Injection volumes of directly injected samples were varied to obtain a suitable detector response comparable to an amount of polymer equivalent to that which was injected using the redissolved samples. Monodisperse polystyrene standards from Waters and Polymer Laboratories with known peak molecular weights ($3 \times 10^3-10^6$) were used to calibrate the instrument. Absolute molecular weights of the polymer were obtained from the molecular weights relative to polystyrene using universal calibration and the Mark-Houwink-Sakaruda parameters $K = 1.1 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.725$ for polystyrene,[16] and $K = 7.26 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.716$ for pV*neo*D, as determined below.

It has been established that reliable k_p values from PLP can only be obtained if certain consistency criteria are fulfilled.[5] Only data that fulfilled all of the following criteria were used in determining k_p: (1) there is another point of inflection present at twice the molecular weight of the first (higher overtones were also observed in some experiments), and the value of k_p obtained is independent of the pulse repetition rate; (2) experiments were also carried out with various initiator concentrations and laser pulse energies to confirm that the measured k_p values were independent of these quantities.

Determination of Mark−Houwink−Sakaruda Parameters. Mark−Houwink−Sakaruda parameters for poly(vinyl *neo*-decanoate) were determined for low-conversion bulk-polymerized vinyl *neo*-decanoate using GPC with an on-line differential viscosity detector and differential refractive index detector (Viscotek Model 250). The reason that the sample was made at low conversion was to reduce any possibility of branching and cross-linking, which would give rise to incorrect MHS values. Four samples of pV*neo*D were prepared using the PLP method outlined above at pulse repetition rates of 30, 10, and 1 Hz, and a broad moleculer weight sample of pV*neo*D was also prepared by thermal initiation with AIBN, for evaluation of the MHS parameters.

The column set consisted of a 5.0 μm bead-size guard column, followed by three fixed bead-size columns (Polymer Laboratories, 5 μm, 10^6, 10^5, and 10^3 Å pore size) and an inline filter (0.2 μm). HPLC-grade tetrahydrofuran was used as eluent, delivered at a constant flow of 1.0 mL min^{-1}. Solutions of the polymer in THF were loaded onto the columns with an autoinjector (Shimadzu SCL 10A). Monodisperse polystyrene standards with known peak molecular weights from Tosh Corp. (TSK, $1.8 \times 10^4-2.9 \times 10^6$) and Polymer Laboratories ($1.3 \times 10^3-3 \times 10^6$) were used to calibrate the instrument. Dioctyl phthalate was added to samples as a flow rate marker. Data were collected and analyzed using Polymer Laboratory Calibre version 6.0 GPC/SEC software.

The inter-detector delay (IDD) is not handled correctly by the commercial software, and special treatment of this was found to be essential to make reliable use of the multiple-detection facility.[17] The method used in the commercial software to calculate intrinsic viscosity from the detector signals is to shift the chromatograms, in an attempt to align equivalent "slices" by using a single fixed estimate of the IDD. However, the IDD appears to depend on molecular wieght and is not constant. To avoid this problem, the method of Suddaby and Sanayei[18] was used. In this method, the detectors are calibrated independently and thus the need for the additional IDD parameter is eliminated. This is important since the error associated with estimation of this parameter is large. Analysis of an unknown is then done by "slice-matching" hydrodynamic volumes in these separate calibration curves.

Results and Discussion

Resolution of Isomers. Gas chromatography analysis of the monomer as supplied shows that the mixture

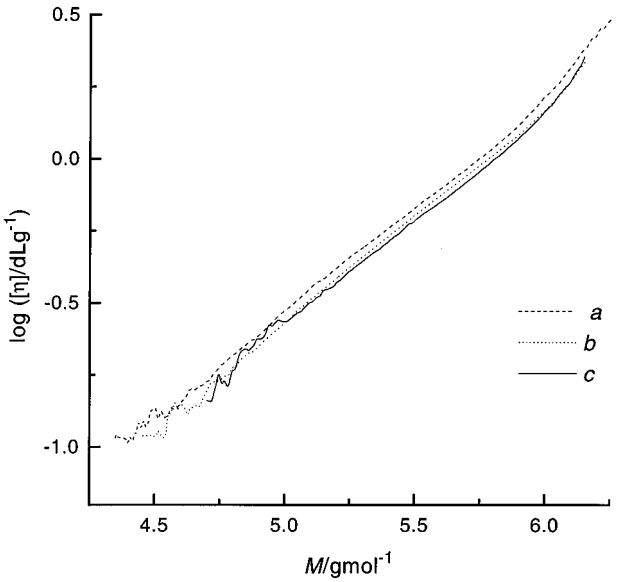

Figure 1. MHS plot of pV*neo*D samples: (a) polymer prepared using PLP; (b) polymer prepared using AIBN, 200 μL injection of 5 mg/mL solution; (c) 100 mL injection of 2.5 mg/mL solution of the same polymer.

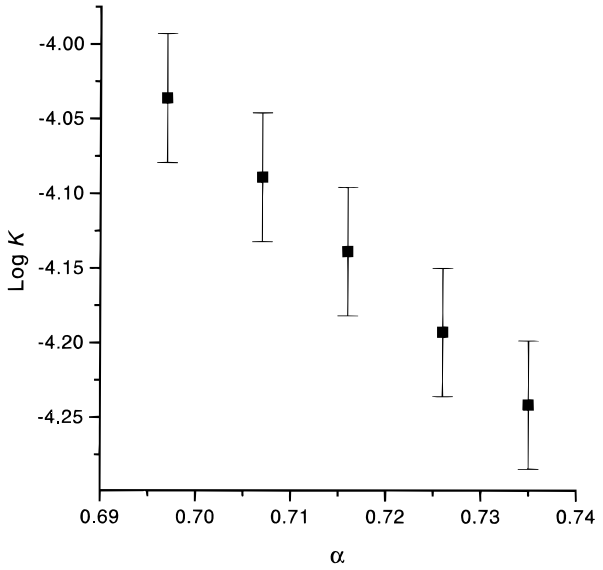

Figure 2. 95% confidence interval for the MHS parameter α and corresponding 95% confidence intervals for *K*, for pV*neo*D.

contains at least six of the 23 possible isomers of V*neo*D, resolved into two main groups.

No attempts were made to resolve the isomers in sufficient amounts to determine k_p of individual isomers. It was assumed that the differences in these individual k_p values was likely to be smaller than the error, typically 10%, in experimentally determined average k_p and would not yield more useful data for the following reasons. The degree of branching of alkyl substituents separated by more than three bonds from the reacting moiety will have little electronic effect at the reaction site and hence on the activation energy (E_a).[19] In addition to results from accurate quantum calculations,[19] an insight into the size of this effect can be obtained from the substituent constants for para *tert*-butyl and methyl substituents (−0.197 and −0.170) for the Hammett equation, which suggests that even the size of the alkyl groups will have little effect on E_a.[20,21] In addition, the relative remoteness of the alkyl group from the radical center suggests (when comparing with data for changing the ester groups in methacrylates, as shown in Table 2) that changes in the structure of R and R′ should have only a very small effect on the frequency factor; indeed, as shown in Figure 6 and Table 2, we have found that the Arrhenius parameters for the V*neo*D mixture are close to those for vinyl acetate even though there is a large difference in mass and structure of the acid moiety. Finally, at a pragmatic level, the k_p value obtained for the isomers will represent an *average* L_0 value (in the Mayo−Lewis sense) applicable to the isomer mixture and so can be properly used to interpret kinetic data for the commercial product.

While polymerization of the mixture is strictly a copolymerization of a number of different monomers, as k_p is not expected to vary significantly between isomers and the product is expected to be a random copolymer with a composition that does not vary with conversion, the polymerization can be treated as a homopolymerization with a k_p that is equal to the average k_p.

Mark−Houwink−Sakaruda Parameters. The relationship between intrinsic viscosity and molecular weight was determined for each of the samples of low-conversion bulk-polymerized pV*neo*D, using GPC with on-line diferential viscometry detection. Eleven repeat experiments were carried out for the sample of polymer prepared using thermal initiation at two different concentrations (5 and 2.5 mg/mL) and injection volumes (200 and 100 μL). While there were significant differences between experiments, the results appeared to be independent of MWD and the amount of injected polymer. A plot of the logarithm of intrinsic viscosity as a function of the logarithm of the molecular weight for three experiments is shown in Figure 1. Results from the other experiments are similar with a very small variation in the slope (α) and a large variation in the intercept (log *K*). The data were found to fit the relationship $\log_{10}[\eta] = \log_{10}(7.26 \times 10^{-5}\ \mathrm{dL\ g^{-1}}) + 0.716 \log_{10} M$ for M between 2×10^4 and 10^6. As the values of α and *K* are highly correlated, it would at first sight appear desirable to construct a 95% joint confidence interval (JCI) for the values of *K* and α rather than assign an error to each parameter. However, constructing a JCI from the combined data leads to a larger estimated error in α than is seen in the experimental variation from data such as Figure 1. To avoid this, the mean and 95% confidence interval (1.96σ) for α were calculated; then for five values of α within this range, the mean and 95% confidence interval for values of *K* were calculated and are shown in Figure 2.

Molecular Weight Distributions. PLP/MWD data were obtained over the range −21 to +21 °C, which fulfilled the required PLP consistency criteria. Each MWD shows a clear point of inflection on the low molecular weight side of the distribution and a second point of inflection corresponding to polymer chains that terminate after two subsequent pulses at approximately twice L_0. Third and fourth overtones are also present in some MWD. An example of an acceptable MWD, with third and fourth overtones, is shown in Figure 3.

Figure 4 shows the values of k_p obtained at two different pulse repetition rates (20 and 30 Hz). The data fit the consistency criteria requiring k_p to be independent of pulse frequency. It can be seen in Table 1 that the values for k_p are also independent of pulse energy, initiator, and initiator concentration. Arrhenius parameters and their confidence intervals were obtained by least-squares fitting the data, as recommended by

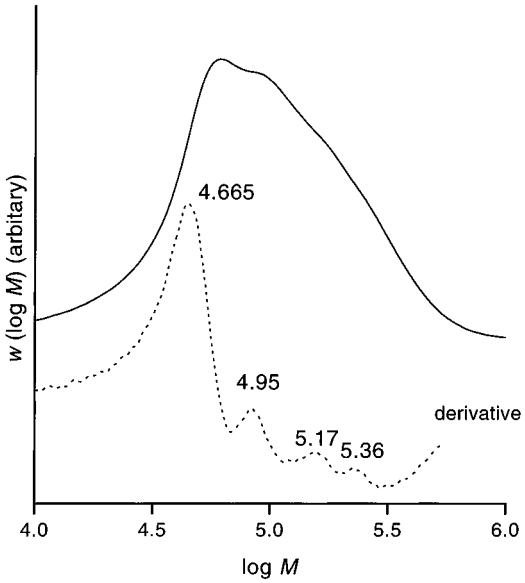

Figure 3. MWD of the product of pulsed laser polymerization of vinyl *neo*-decanoate, at 11 °C with *Irgacure 651* (1×10^{-3} mol dm^{-3}) as the photoinitiator and a pulse energy of 20 mJ and pulse frequency of 30 Hz.

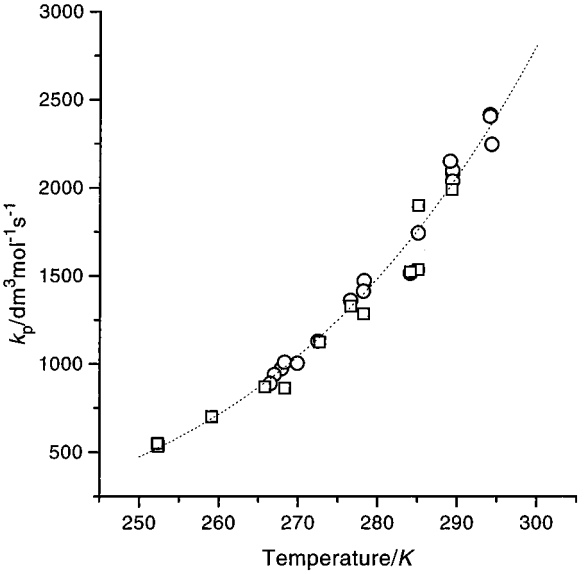

Figure 4. Propagation rate coefficients of free radical polymerization of vinyl *neo*-decanoate; experiments carried out at repetition rates of 30 Hz (○) and 20 Hz (□).

van Herk.[22] The Arrhenius plot is shown in Figure 5 with 95% confidence limits extrapolated to other reaction temperatures; the extrapolated values are those calculated from all pairs of values of the Arrhenius frequency factor and activation energy A and E_a in the JCI. E_a and A for free-radical propagation of V*neo*D were found to be 22.2 kJ mol^{-1} and $10^{7.31}$ dm^3 mol^{-1} s^{-1}, respectively. Two 95% joint confidence intervals for the Arrhenius parameters are shown in Figure 6, using the two extreme values of K and α from Figure 2.

A comparison of the Arrhenius parameters with those of other monomers is shown in Table 2. The values for the present monomer are similar to those of the only other vinyl alkanoate monomer, vinyl acetate, for which there are reliable values.[23] This is consistent with the reported reactivity ratios for copolymerization with VAc being near unity ($r_{VAc} = 0.99$, $r_{VneoD} = 0.92$). As expected from theory,[19,24] the size of the alkyl substituents has little effect on E_a for the vinyl alkanoates, with the reported E_a for VAc (20.5 kJ mol^{-1}) slightly lower than that for V*neo*D (22.2 kJ mol^{-1}). The frequency factor for V*neo*D is similar to that of the reported value for VAc ($10^{7.31}$ and $10^{7.16}$ dm^3 mol^{-1} s^{-1}, respectively). Whether or not these relatively small differences are significant depends, of course, on the JCIs for

Table 1. Pulsed Laser Polymerization Conditions and Measured k_p[a]

sample. no.	log M at point of inflection	temp/ °C	repetition rate, Hz	initiator conc/mmol dm^{-3}	pulse energy/mJ	k_p/dm^3 mol^{-1} s^{-1}
1	4.785	16.3	30	3	15	2082
2	4.788	16.3	30	3	15	2097
3	4.775	16.3	30	3	25	2037
4	4.464	−5.2	30	3	15	971
5	4.449	−6.1	30	3	15	938
6	4.426	−6.6	30	3	15	888
7	4.923	12	20	3	15	1899
8	4.830	12	20	3	25	1535
9	4.709	12	30	2	15	1743
10	4.941	16.2	20	2	15	1989
11	4.593	−7.3	20	2	15	869
12	4.706	−0.4	20	2	15	1138
13	4.772	3.5	20	3	15	1328
14	4.606	3.5	30	3	15	1360
15	4.527	−0.6	30	2	15	1128
16	4.799	16	30	2	15	2150
17	4.847	21	30	2	15	2415
18	4.845	21	30	3	5	2405
19	4.481	−4.8	30	3	10	1009
20	4.588	−4.8	20	3	10	862
21	4.504	−14	20	3	15	701
22	4.639	5.1	30	3	15	1471
23	4.477	−3.2	30	1	10	1003
24	4.621	5.1	30	1	10	1412
25	4.475	5.1	20	1	10	1284
26	4.816	21.2	30	3	10	2245
27	4.388	−20.7	20	2	10	532
28	4.401	−20.8	20	2	10	549
29*	4.648	11	30	1	20	1514
30*	4.827	11	20	1	20	1522

[a] Initiator in all experiments is benzoin, except for those marked *, where the initiator is Irgacure 651.

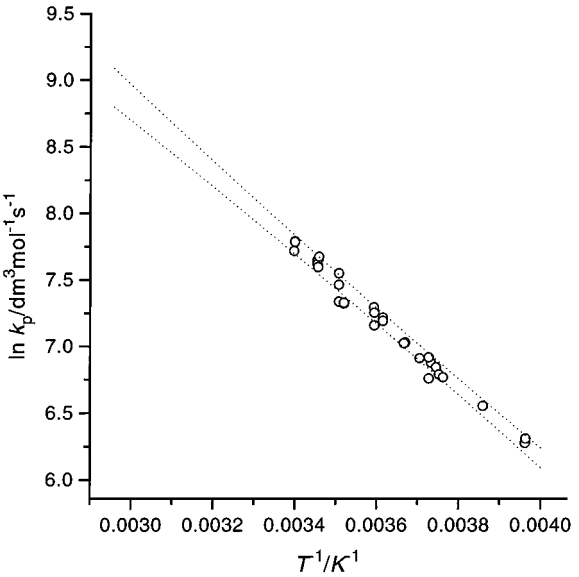

Figure 5. Arrhenius plot of propagation rate coefficients with 95% confidence intervals, together with values extrapolated to other temperatures.

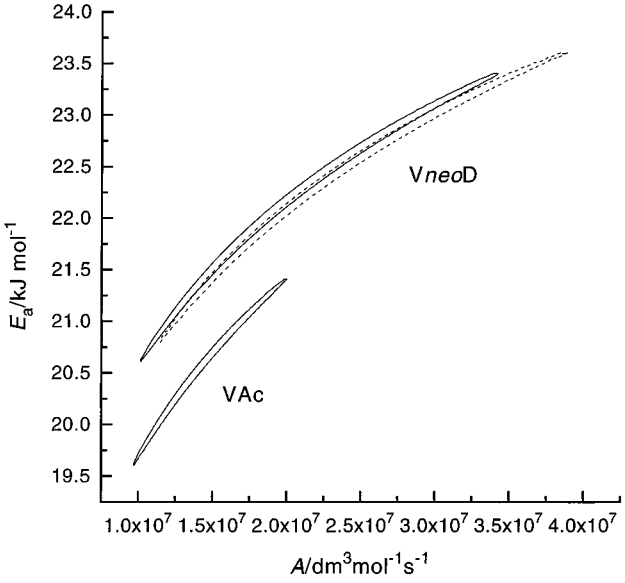

Figure 6. 95% confidence limits of pairs of values of E_a and A for the propagation rate coefficient of free radical polymerization of vinyl *neo*-decanoate (present data) and of vinyl acetate (supplementary data from ref 23).

these quantities, which are shown in Figure 6 and show that these differences are indeed statistically significant, as the intervals do not overlap. It is unclear as to whether the small but significant difference is due to a difference in E_a or A, as the 95% confidence intervals for the individual parameters overlap.

One possible origin for these differences is lower E_a is an electronic effect due to the hydrogens α to the carbonyl goup in VAc, which are not present in V*neo*D. Although these hydrogens are are a number of bonds from the vinyl group, they are slightly acidic due the presence of the ester group that is bonded directly to the vinyl group. It is possible then that the electronic effect of these hydrogens at the vinyl group may be large enough to affect E_a.

Differences in A may be due to the large size difference between the acetate and *neo*-decanoate groups; this could cause a small but significant difference in the hindered rotors in the transition state for propagation, which dominate the value of the frequency factor.[25] As an example of this last effect, it is likely that the higher value of A for an acrylate compared to that of the corresponding methacrylate arises from the change in hindrance caused by the methyl group on the side chain.[26] Relatively accurate semiempirical means of quantifying this for large monomers such as vinyl *neo*-decanoate are becoming available,[24] and application of this methodology to the differences seen here is a useful area for future work.

Table 2 shows that there is little difference between E_a of the vinyl esters and methacrylates even though the carbonyl group is conjugated with the alkene in the methacrylates. The only acrylate in the group, butyl acrylate, has a much lower E_a than that of the vinyl esters or methacrylates. Where there is similar conjugation, as with styrene, E_a has a much higher value, as would be expected if conjugation lowers the energy of reactants. Unfortunately, the current status of accurate quantum calculations[24,25] is such that no *a priori* estimate of E_a can yet be made for molecules of this size, and certainly not to an accuracy of 2 kJ mol^{-1}.

A particularly interesting point is why V*neo*D gives such excellent PLP data, in the sense that it is relatively easy to find conditions for the PLP consistency criteria to be obeyed [higher overtones (even third and fourth!) in the right positions, and independence of pulse frequency], while it has been found very difficult to obtain consistent data with vinyl acetate, even though the propagation rate coefficients are very similar.[13] A number of reasons have been put forward why consistent PLP data are difficult to obtain for vinyl acetate and the acrylates.[12,13,23,26] These monomers all have a high k_p; however, because of the similarity of the k_p values for VAc and vinyl *neo*-decanoate, it is apparent that this problem cannot simply be due to a high k_p. It has been suggested[27] that the problem may arise from a combination of a high propagation rate and high rate of chain transfer to monomer, resulting in a very small number fraction of polymer of degree of polymerization L_0 and a large amount of lower molecular weight polymer: Beuermann *et al.* suggested that as a rough

Table 2. Values of Arrhenius Parameters for Vinyl *neo*-Decanoate and Some Other Monomers[a]

monomer	$\log_{10}(A$/dm^3 mol^{-1} s$^{-1})$	E_a/kJ mol^{-1}	k_p °C/10^{-2} dm^3 mol^{-1}s^{-1}	reference
vinyl *neo*-decanoate	7.31	22.2	52	present work
vinyl acetate	7.16	20.7	65	23
methyl methacrylate	6.43	22.4	6.5	31
ethyl methacrylate	6.51	22.8	6.7	23
n-dodecyl methacrylate	6.44	21.5	9.2	23
n-butyl methacrylate	6.39	21.8	7.3	23
i-butyl methacrylate	6.47	22.5	6.8	23
n-butyl acrylate	7.26	17.4	280	26,27
styrene	7.63	32.5	2.4	5
chlorobutadiene	7.3	26.6	10	12

[a]All data are obtained from PLP experiments that satisfy the consistency criteria for this technique.

rule of thumb, if DP_{tr}, the average degree of polymerization to which a radical propagates before undergoing a transfer event, is less than twice L_0, a suitable MWD cannot be obtained. Further investigation of this (including the possibility of interference from adventitious chain-transfer agents, whose presence can be measured by the time evolution of the number MWD with steady illumination[28−30]) is anticipated.

Conclusions

Arrhenius parameters for the (average) k_p of a mixture of isomers of V*neo*D were found to be $A = 10^{7.31}$ dm^3 mol^{-1} s^{-1} and $E_a = 22.2$ kJ mol^{-1}; the values for individual isomers are not expected to vary significantly from these averages. The data analysis required careful quantification of the uncertainties in the Mark−Houwink−Sakaruda parameters used to interpret the GPC data, these parameters being obtained by triple-detector size-exclusion chromatography. The Arrhenius parameters are similar to those reported for VAc, with some overlap of, but a statistically significant difference in, the 95% joint confidence interval. The results show that the alkyl groups of the acid moiety have only a small effect on the propagation rate coefficient of vinyl alkanoates. This contrasts with larger differences in the activation energies and frequency factors between butyl acrylate and the methacrylates but is consistent with the small variation in k_p with alkyl substituents in the methacrylate series. The present data for k_p will prove useful for later mechanistic studies of emulsion polymerizations of systems containing this monomer.

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