quaternization of 1.83 g. of 2-benzoylpyridine with 2.01 g. of *p*-methoxybenzyl bromide[10] was carried out in six days at room temperature. To the crude salt 60 ml. of hydrogen fluoride was added and allowed to evaporate slowly in the usual way. The residue was dissolved in water and exactly one-half of the solution was converted to the reineckate by addition of ammonium reineckate. The rose-colored precipitate was washed with ethanol and ether, m.p. 158–159°, yield 1.12 g. (36%). The melting point of the analytical sample (recrystallized from ethanol and ether) was unchanged.

A sample of **1-(4-methoxybenzyl)-2-benzoylpyridinium reineckate** prepared from the bromide gave the identical melting point, mixed melting point and infrared spectra.

Anal. Calcd. for $C_{24}H_{24}CrN_7O_2S_4$: C, 46.21; H, 3.88; N, 15.72. Found: C, 46.31; H, 3.83; N, 16.09.

11-Methylacridizinium Perchlorate (X, R = H).—The quaternization of 1.21 g. of 2-acetylpyridine with 1.71 g. of benzyl bromide in the presence of 1 ml. of dimethylformamide was carried out in a 4-oz. polyethylene bottle at 10° for 23 days. Ether was added to precipitate the salt (as an oil) and the ether decanted. To the small quantity of oil obtained, 60 ml. of liquid hydrogen fluoride was added and cyclization and isolation carried out as usual. The perchlorate was obtained from ethanol as blunt orange-brown needles, m.p. 239–241°, yield 0.10 g. (3%). The analytical sample melted at 243–244.5°; λ_{max} (log ϵ): 243 (4.61), 250 (4.60), 365 (4.04), 382 (4.11), 402 (4.00); λ_{min}, 247 (4.58), 313 (3.08), 372 (3.93), 391 mμ (3.82).

Anal. Calcd. for $C_{14}H_{12}ClNO_4$: C, 57.25; H, 4.12; N, 4.77. Found: C, 57.54; H, 3.86; N, 4.80.

6-Methyl-11-phenylacridizinium Perchlorate.—Quaternization of 1.83 g. of 2-benzoylpyridine by 1.85 g. of α-bromoethylbenzene in 1.0 ml. of dimethylformamide was carried out at 10° for 222 days. The crude orange oil which formed was washed with ether and cyclized in 100 ml. of hydrogen fluoride in the usual way. After all the hydrogen fluoride had evaporated the residue was taken up in water and filtered. The addition of perchloric acid to the filtrate gave a light yellow precipitate which after separation and crystallization from ethanol, consisted of large yellow irregular crystals, m.p. 218.5–220°, yield 0.32 g. (8.6%). The analytical sample melted from 222–223°; λ_{max} (log ϵ), 249 (4.65), 370 (4.11), 389 (4.09), 410 mμ (4.05); λ_{min}, 318 (3.24), 379 (3.98), 400 (3.90).

Anal. Calcd. for $C_{20}H_{16}ClNO_4$: C, 64.95; H, 4.36; N, 3.79. Found: C, 65.19; H, 4.32; N, 3.71.

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[10] A. Lapworth and J. B. Shoesmith, *J. Chem. Soc.*, **121**, 1397 (1922).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE EASTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Chain Transfer Constants of Vinyl Esters with Toluene[1]

BY C. F. THOMPSON,[2] W. S. PORT AND L. P. WITNAUER

RECEIVED NOVEMBER 6, 1958

Weight average molecular weights have been used to determine chain transfer constants of three vinyl esters with toluene. It has been shown that polyvinyl acetate prepared in varying amounts of toluene has a constant molecular weight distribution $M_w/M_n = K$, leading to a linear relation between $1/P_w$ and (S)/(M). The transfer constant obtained from this relation has been designated C_S', and differs only slightly from the true transfer constant. It has the advantage of being more easily measured in many cases. The vinyl esters have similar reactivities, regardless of the length of the acyl chain, although increased chain transfer to monomer is observed with increasing chain length.

An earlier report on the copolymer reactivity ratios of a number of vinyl esters has shown that all have similar reactivities, regardless of the nature of the acyl portion of the molecule.[3] In the present work, the chain transfer of vinyl acetate, vinyl pelargonate and vinyl stearate with toluene has been studied, the monomers being chosen for the wide variance in the length of the acyl chain. These monomers have been polymerized in the presence of varying amounts of toluene at three temperatures, and activation energy differences and frequency factor ratios have been calculated from the temperature dependence of the chain transfer constants. A new method for evaluating transfer constants by means of weight average molecular weights has been used and found to be theoretically and experimentally justified.

Chain transfer constants are determined by means of the expression

$$1/P_n = C_M + C_S\frac{(S)}{(M)} + C_I\frac{(I)}{(M)} + \frac{k_tR_p}{k_p^2(M)^2} \qquad (1)$$

where P_n is the number average degree of polymerization, R_p is the rate of polymerization, and (S), (M) and (I) are the concentrations of solvent, monomer and initiator. The transfer constants C_M, C_S and C_I represent the ratios of the rate constants for transfer to the rate constant for propagation; *i.e.*, $C_S = k_{Tr.S}/k_p$.[4,5]

This expression may be simplified by the proper choice of experimental conditions. The term involving the initiator transfer constant may be reduced to zero by using azobisisobutyronitrile, which does not undergo transfer.[5] Furthermore in polymerizations initiated bimolecularly, the steady state treatment yields for the last term $(k_ik_t)^{1/2}(I)^{1/2}/k_p(M)^{1/2}$ which may be held constant over a series of polymerizations by maintaining a constant (I)/(M) ratio. Since the term C_M is constant by nature, the simplified expression results

$$1/P_n = C_S\frac{(S)}{(M)} + 1/P_0 \qquad (2)$$

By plotting the reciprocal degree of polymerization

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[1] This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.

[2] The paper is based on portions of a thesis submitted by C. F. Thompson to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Reprint requests should be addressed to Polymer Research, 107 Noyes Laboratory, University of Illinois, Urbana, Ill.

[3] C. S. Marvel and W. G. DePierri, *J. Polymer Sci.*, **27**, 39 (1958).

[4] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) S. Basu, J. Sen and S. R. Palit, *Proc. Roy. Soc. (London)*, **A214**, 247 (1952); (c) B. Baysal and A. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

[5] S. R. Palit and S. K. Das, *Proc. Roy. Soc. (London)*, **A226**, 82 (1954).

versus the initial solvent:monomer ratio, and limiting the reactions to low conversion, it is possible to determine from the slope the chain transfer constants of solvent–monomer pairs from a series of polymerizations. These transfer constants reveal the activity of monomers and solvents in a manner similar to copolymer reactivity ratios.

The study of transfer constants in the past has been somewhat hampered by the necessity for using number average molecular weights. Osmotic pressure measurements are often not convenient, and in the case of many polymers, equations relating viscosity to number average molecular weight are not available. However, it is shown in this study that weight average molecular weights provided by light scattering measurements are reliable for the determination of modified transfer constants which closely approximate the true transfer constants.

Experimental

Purification of Reagents.—a. Vinyl acetate (Matheson Co., Inc.[6]) was distilled in a nitrogen atmosphere, allowed to reflux briefly in the presence of a small amount of benzoyl peroxide, and then redistilled under nitrogen from residual polymer. The fraction boiling at 72–72.5° was collected. A negative Schiff test indicated freedom from aldehydes.

b. Pelargonic acid (Emery Industries, Inc.[6]) was purified by esterifying with ethylene glycol, thereby removing any dibasic acids as an undistillable residue. The distilled ester was hydrolyzed, and vinyl pelargonate prepared from the acid in 71% yield by interchange with vinyl acetate.[7] This material was redistilled, and the fraction boiling at 65° (1.5 mm.) was collected $n^{22.0}\text{D}$ 1.4320.

c. Vinyl stearate (Air Reduction Co.[6]) was vacuum distilled in a nitrogen atmosphere, b.p. 166° (1.5 mm.), and then recrystallized three times from acetone or ethyl acetate to m.p. 35°.

d. Reagent grade toluene was washed successively with concentrated sulfuric acid and aqueous sodium carbonate, dried, and distilled in an atmosphere of nitrogen.

Preparation of Polymers.—All polymerizations were run in four-ounce screw-capped bottles immersed in a water-bath at a temperature controlled to ±0.05°. Monomer, initiator and solvent were weighed separately and added to the bottles, which were flushed with nitrogen for 30 seconds before capping. Azobisisobutyronitrile was used to initiate polymerization, and a constant initiator:monomer molar ratio of 6.6×10^{-4} was used in all cases. The time required to reach 10% conversion was judged by pilot runs. At the end of this time, the bottles were cooled quickly and their contents poured into precipitating reagents.

Purification of Polymers.—Polyvinyl acetate was precipitated by pouring into cold (−10 to 0°) low boiling petroleum ether. It was reprecipitated three times from benzene into cold, well stirred petroleum ether, and finally freeze-dried from benzene solution.

In a similar manner, polyvinyl pelargonate was reprecipitated three times from benzene into cold methanol, and polyvinyl stearate from benzene into acetone. The semi-fluid polyvinyl pelargonate was dried by applying high vacuum to its benzene solution, while the solid, powdery polyvinyl stearate was dried in air on the filter.

Determination of Molecular Weights.—Light scattering measurements, at angles from 135 to 30° to the primary beam, were made with a Brice–Phoenix photometer[8] using a cylindrical scattering cell at wave length 546 mμ. The refractive increment was determined in a differential refractometer. The average d*n*/d*c* values were 0.103 ± 0.001 for polyvinyl acetate in acetone, 0.069 for polyvinyl pelargonate in tetrahydrofuran, and 0.071 for polyvinyl stearate in tetrahydrofuran. All solutions used were first clarified by centrifugation and then passed through ultrafine sintered glass filters.

Viscosity measurements were made in an Ostwald viscometer having efflux times of 100 seconds for tetrahydrofuran and 78 seconds for acetone. Each sample was run at four concentrations, and in nearly all cases the relative viscosities were between 1.1 and 2.0. Intrinsic viscosities were determined by extrapolating linear plots of η_{sp}/c *vs.* c to zero concentration.

For weight average determinations, all viscosities were measured in tetrahydrofuran at 30°. The molecular weight relations determined from light scattering measurements are

for polyvinyl acetate, $(\eta) = 1.38 \times 10^{-4}\ M_{\text{w}}^{0.70}$
for polyvinyl pelargonate, $(\eta) = 2.01 \times 10^{-4}\ M_{\text{w}}^{0.62}$
for polyvinyl stearate, $(\eta) = 5.04 \times 10^{-4}\ M_{\text{w}}^{0.52}$

For number average molecular weights of polyvinyl acetate, viscosities were measured in acetone at 25°, and the relation $(\eta) = 1.88 \times 10^{-4}\ M_{\text{w}}^{0.69}$ was used.[9] This is based on fractionated polyvinyl acetate, and appears to be the most suitable of the many in the literature.

From the molecular weight data, reciprocal degrees of polymerization were calculated and plotted against the initial (S)/(M) ratios. Chain transfer constants were determined by measuring the slopes of these lines.

Discussion of Results

Use of Weight Average Data.—It can be shown that in polymerizations in which chain transfer terminates nearly all chains, the molecular weight distribution is given by $M_{\text{w}}/M_{\text{n}} = 1 + p$, where p is the instantaneous probability that a growing chain will add another monomer unit before terminating.[10] If the ratio (S)/(M) does not change appreciably during the polymerization, p will remain effectively constant, and the expression may be rewritten $M_{\text{w}}/M_{\text{n}} = K$, where $1.0 < K < 2.0$. Substituting this expression in the chain transfer expression, a new relation results.

$$1/P_{\text{w}} = \frac{C_{\text{S}}}{K}\frac{(\text{S})}{(\text{M})} + \frac{1}{KP_0} \qquad (3)$$

Defining the term C_{S}/K as C_{S}', the weight average transfer constant, the final equation may be written

$$1/P_{\text{w}} = C_{\text{S}}'\frac{(\text{S})}{(\text{M})} + \frac{1}{KP_0} \qquad (4)$$

Since K may vary between 1.0 and 2.0, the weight average transfer constant may be as low as one-half of the true transfer constant. However, in the case studied, the variance was not this great, and in many practical applications such a variance is of little significance.

That this proposed linear relationship $M_{\text{w}}/M_{\text{n}} = K$ does not change detectably with increasing solvent concentration was verified experimentally in the case of polyvinyl acetate, for which constants relating viscosity to both number average and weight average molecular weights were available. A series of polymers of varying molecular weights was prepared by polymerizing in the presence of varying amounts of toluene, and both averages were determined. The results are given in Table I and Fig. 1. In the plot of M_{n} *vs.* M_{w}, all points lie on a straight line passing nearly through the origin.

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[6] Reference to commercial products does not constitute a recommendation by the Department of Agriculture over similar products not mentioned.

[7] D. Swern and E. F. Jordan, Jr., *Org. Syntheses*, **30**, 106 (1950).

[8] B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Amer.*, **40**, 768 (1950).

[9] R. H. Wagner, *J. Polymer Sci.*, **2**, 21 (1947).

[10] (a) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334. (b) F. W. Billmeyer, Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1957, p. 245.

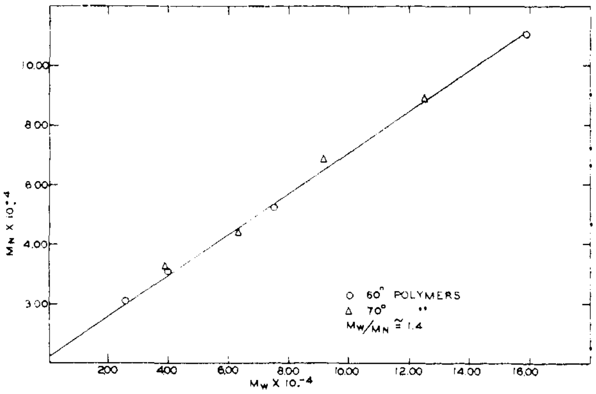

Fig. 1.—Relationship between number-average and weight-average molecular weights of polyvinyl acetate prepared in toluene.

This line is represented by $M_w/M_n \cong 1.4$, the value of K thus falling within the limits predicted above. It should be noted that this distribution is constant over an eightfold solvent concentration range, and also over samples prepared at 60 and 70°. It appears that small temperature changes have little effect on the molecular weight distribution.

TABLE I

MOLECULAR WEIGHTS OF POLYVINYL ACETATE

Sample	(S)/(M)	Conversion, %	M_w	M_n
59-B	0.234	8.8	125,000	88,500
59-C	.351	13.2	91,400	68,600
59-D	.583	13.2	63,600	43,800
59-E	.936	12.5	39,500	32,200
101-A	.234	10.3	159,000	111,000
101-B	.583	10.0	75,000	52,600
101-C	1.168	10.3	40,000	30,800
101-D	1.751	10.0	26,200	20,800

Further justification for the validity of equation 4 lies in the fact that the proposed linear relation between $1/P_w$ and (S)/(M) is found to hold experimentally. Table II gives the experimental conditions and results for the determination of chain transfer constants by the use of weight average data. The plots from which these data are derived were characterized by an increase in both slope and intercept with increasing temperature for each monomer.

These number average measurements on polyvinyl acetate polymerized at 60° show $C_S = 2.16 \times 10^{-3}$ (Table III). Under the same conditions, and using the same viscosity constants, Palit and Das[5] found $C_S = 2.18 \times 10^{-3}$. Weight average measurements on the same samples of polyvinyl acetate yield a value of $C_S' = 1.78 \times 10^{-3}$. Thus it is evident that the weight average value is closely representative of the true transfer constant, although slightly lower as expected from theoretical considerations.

TABLE II

DETERMINATION OF WEIGHT AVERAGE CHAIN TRANSFER CONSTANTS WITH TOLUENE

Sample	Conversion, %	Intrinsic viscosity,[a] dl./g.	(S)/(M)	P_w	$1/P_0 \times 10^{3b}$	$C_S' \times 10^3$
Vinyl acetate, 50°	5.3	0.660	0.234	2280		
	8.0	.527	.351	1520		
	5.0	.398	.584	1020		
	5.3	.256	1.168	541	0.11	1.49
Vinyl acetate, 60°	10.3	.603	0.234	1850		
	10.0	.357	0.584	872		
	10.3	.230	1.168	464		
	10.0	.172	1.751	305	0.15	1.78
Vinyl acetate, 70°	8.8	.512	0.234	1450		
	12.5	.410	.351	1060		
	13.3	.318	.584	739		
	13.3	.228	.936	459	0.21	2.11
Vinyl perlargonate, 50°	6.7	.250	.333	532		
	5.7	.222	.667	408		
	7.3	.188	1.333	336		
	9.0	.161	2.000	262	1.5	1.11
Vinyl pelargonate, 60°	3.0	.240	0.333	498		
	9.3	.175	1.333	299		
	9.0	.149	2.000	231		
	3.7	.117	3.333	157	1.5	1.39
Vinyl perlargonate, 70°	10.6	.209	0.333	398		
	11.7	.190	0.667	342		
	10.6	.156	1.333	248		
	15.0	.136	2.000	200	2.0	1.52
Vinyl stearate, 50°	10.5	.197	0.848	310		
	5.0	.160	1.686	208		
	6.0	.134	2.529	148		
	4.0	.108	4.215	98	1.4	2.07
Vinyl stearate, 60°	5.7	.175	0.848	247		
	7.3	.145	1.686	172		
	7.0	.126	2.529	131		
	4.7	.104	4.215	91	2.3	2.09
Vinyl stearate, 70°	11.0	.179	0.421	259		
	7.5	.156	0.868	198		
	9.0	.118	2.529	116		
	6.3	.098	4.215	81	3.1	2.16

[a] In tetrahydrofuran at 30°. [b] From intercept of $1/P$ *vs.* [S]/[M] plot.

TABLE III

NUMBER AVERAGE CHAIN TRANSFER CONSTANTS OF VINYL ACETATE WITH TOLUENE

Sample	Conversion, %	Intrinsic viscosity,[a] dl./g.	(S)/(M)	P_n	$C_S \times 10^3$
Vinyl acetate, 60°	10.3	0.570	0.234	1290	
	10.0	.340	0.584	612	
	10.3	.235	1.168	358	
	10.0	.179	1.751	242	2.16
Vinyl acetate, 70°	8.8	.487	0.234	1030	
	12.5	.408	.351	798	
	13.3	.300	.584	509	
	13.3	.242	.936	372	2.92

[a] In acetone at 25°.

While it is known that the presence of aromatic solvents in a polymerization reaction often reduces the rate of polymerization due to the formation of stable aromatic radicals,[11,12] this has little effect on the above experiments. Theory requires constancy of the term $R_p/(M)^2$ across the series; conceivably, a decrease of R_p proportional to the amount of toluene present could lead to a reduction in the slope

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(11) G. M. Burnett and H. W. Melville, *Disc. Faraday Soc.*, **2**, 322 (1947).

(12) W. H. Stockmayer and L. H. Peebles, Jr., THIS JOURNAL, **75**, 2279 (1953).

of the $1/p$ *vs.* (S)/(M) plots. However, the literature shows that this reduction in the rate, although large between bulk polymerizations and polymerization in the presence of moderate amounts of solvent, is small across a fairly large range of (S)/(M) values after the initial drop.[11] Furthermore, the amount of initiator used in these experiments was deliberately kept low to minimize the contribution of the $R_p/(M)^2$ term. Polymerizations of vinyl acetate and vinyl stearate in which the initiator concentration was varied over an eightfold range at this low level showed that the contribution of this term was negligible; polyvinyl acetate showed only a slight tendency toward upward curvature of the $1/p$ *vs.* (S)/(M) plots with increasing initiator concentration, and polyvinyl stearate showed practically none.

Reactivities of Vinyl Esters.—The values of C_S' for polyvinyl acetate, pelargonate and stearate are given in Table II. At a given temperature, the values for all three polymers are closely grouped, suggesting again that the length of the acyl chain has little effect on reactivity. At 60°, for example, there is less than a twofold difference in the transfer constants for the three monomers. In contrast, vinyl acetate ($C_S' = 1.78 \times 10^{-3}$) is more than 100 times as active as styrene ($C_S = 1.2 \times 10^{-5}$) at the same temperature. That this difference is due entirely to the lower activition energy difference in the case of vinyl acetate is shown by plotting of log C_S' *vs.* $1/T$. In these plots, since $C_S = k_{\mathrm{Tr,S}}/k_p$, the quantities A_{Tr}/A_p and $E_{\mathrm{Tr}} - E_p$ may be determined from the intercept and slope. The results are summarized in Table IV.

TABLE IV

RESULTS OF ARRHENIUS PLOTS

Monomer	$A^{\mathrm{Tr}}/A^{\mathrm{p}}$[a]	$E_{\mathrm{Tr}} - E_p$ in $k_{\mathrm{cal.}}$/mole
Vinyl acetate	5.2×10^{-1}	3.8
Vinyl pelargonate	2.4×10^{-1}	3.4
Vinyl stearate	4.4×10^{-3}	0.5

[a] Calculated from $E_{\mathrm{Tr}} - E_p$ and log C_S' at 60°.

At 60° for transfer between styrene and toluene, $A_{\mathrm{Tr}}/A_p = 55.6$ and $E_{\mathrm{Tr}} - E_p = 10.1$.[13] Thus, although the frequency factor ratio is less favorable, the lower activation energy difference for the vinyl esters makes them more susceptible to transfer than styrene.

If the plots of log C_S' *vs.* $1/T$ are treated in terms of absolute rate theory, the values given in Table V result.

TABLE V

FREE ENERGY AND ENTROPY OF ACTIVATION DIFFERENCES AT 60°

Monomer	$\Delta F^{\ddagger}_{\mathrm{Tr}} - \Delta F^{\ddagger}_{\mathrm{p}}$, kcal./mole	$\Delta S^{\ddagger}_{\mathrm{Tr}} - \Delta S^{\ddagger}_{\mathrm{p}}$, e.u.
Vinyl acetate	4.2	− 1.3
Vinyl pelargonate	4.4	− 2.9
Vinyl stearate	4.1	−10.7

Although the differences in the free energies of activation for the two competing reactions (transfer and propagation) are unaffected by the length of the acyl chain, the differences in the entropies of activation markedly decrease. Further interpretation of these data is questionable without a determination of absolute reaction rate constants. Moreover, any interpretation must be tempered by consideration of the narrowness of the temperature range studied and of the inherent experimental errors.

Chain Transfer with Monomer.—An increase in chain transfer with monomer is to be expected in passing from vinyl acetate to vinyl stearate, due to the increase in the number of hydrogens in the acyl chain.[14] This increase is evident from a consideration of the intercepts of plots of $1/P_w$ *vs.* [S]/[M]. Passing from vinyl acetate to vinyl stearate at 60°, the term $1/P_0$ increases from 0.15×10^{-3} to 1.5×10^{-3} to 2.3×10^{-3}. This cannot be due to the R_p/M^2 term, which actually decreases across this series. Hence the increase of $1/P_0$ reflects the increase of chain transfer with monomer across the series. This greater amount of chain transfer with monomer prevents the preparation of very high molecular weight polymers from long chain monomers, even in the absence of solvents.

Conclusions

In summary it may be said that three factors indicate that weight average molecular weights may be used to obtain reliable values for chain transfer constants: (1) there is a constant molecular weight distribution $M_w/M_n = K$ over the range of solvent concentrations studied, (2) the predicted linear relationship between $1/P_w$ and (S)/(M) does exist, and (3) there is only a slight difference in the values of the chain transfer constant determined by number average and weight average methods. It must be borne in mind that in the limiting case, the value obtained by weight average measurements may be only one-half of the true value. This limit can never be realized, of course, since it requires that $p = 1$, implying infinite polymerization. Practically, there will be little difference between C_S and C_S'. In many cases, then, the lack of number average data or the greater ease of determining light scattering molecular weights may dictate the use of these weight average transfer constants. Such constants, although not absolute, may be used with some confidence in relating various systems.

In considering the reactivities of the three vinyl esters, it can only be said that they are strikingly similar. It appears that the small differences noted are correlated with structure only in the sense that entropy of activation differences increase negatively as the chain length increases. More importantly, the longer chain monomers exhibited a greater amount of chain transfer with monomer, thus limiting the molecular weights attainable.

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(13) Calculated from data of R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947).

(14) A. Buselli, M. Lindemann and C. Blades, *J. Polymer Sci.*, **28**, 485 (1958).