

Chain Transfer for Vinyl Monomers Polymerized in *N*-Allylstearamide

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Synopsis

Apparent transfer constants have been determined for styrene, methyl methacrylate, vinyl acetate, and diethyl maleate polymerized in *N*-allylstearamide at 90°C. Regression coefficients for transfer were: methyl methacrylate, 0.301×10^{-3} ; styrene, with no added initiator, 0.582×10^{-3} ; styrene, initiated with benzoyl peroxide, 0.830×10^{-3} ; vinyl acetate, 62.01×10^{-3} ; and diethyl maleate, 2.24×10^{-3} . Rates of polymerization were retarded for both styrene and methyl methacrylate. Vinyl monomer and comonomer disappearance followed an increasing exponential dependence on both initiator and monomer concentration. Although degradative chain transfer probably caused most of the retardation, the cross-termination effect was not eliminated as a contributing factor. Rates for the vinyl acetate copolymerization were somewhat retarded, even though initiator consumption was large because of induced decomposition. The kinetic and transfer data indicated that the reactive monomers added radicals readily, but that rates were lowered by degradative chain transfer. Growing chains were terminated at only moderate rates of transfer. Unreactive monomers added radicals less easily, producing reactive radicals, which transferred rapidly, so that molecular weights were lowered precipitously. Although induced initiator decomposition occurred, rates were still retarded by degradative chain transfer. A simple empirical relation was found between the reciprocal number-average degree of polymerization, $1/\bar{X}_n$, and the mole fraction of allylic comonomer entering the copolymer F_2 , which permitted estimation of the molecular weight of copolymers of vinyl monomers with allylic comonomers. This equation should be applicable when monomer transfer constants for each homopolymer are known and when osmometric molecular weights of one or two copolymers of low allylic content have been determined.

INTRODUCTION

It has been known for a long time that copolymers of vinyl monomers with allylic comonomers generally have substantially lower molecular weights than entirely vinyl copolymers of the same molar composition. This is a consequence of the ease of hydrogen abstraction from allylic monomers by chain radicals,¹ which terminates their growth, and lowers the molecular weights of the copolymers. Rates of copolymerization are also abnormally lowered because of degradative destruction of the resonance-stabilized allylic radicals. Qualitative demonstrations of these

effects were found in copolymerization studies of styrene and allyl chloride,² acrylonitrile and allyl alcohol,³ maleic anhydride and allyl acetate,⁴ and ethyl acrylate and allyl chloride.⁵ In examples from the patent literature, allylic comonomers were used to control molecular weight in copolymers^{6,7} and to produce telomers.^{8,9} Using a more quantitative approach to allylic transfer, several authors have determined transfer constants for selected vinyl monomers in the presence of allyl monomers considered as solvents. In this way, vinyl acetate was studied in allyl chloride, allyl acetate, and methallyl chloride;¹⁰ and ethylene,¹¹ methyl methacrylate,¹² and styrene¹³ in 1-olefins. In general, the magnitude of the constants increased with vinyl radical reactivity.

As part of a general investigation of the use of long-chain vinyl monomers in homopolymerization and copolymerization, apparent transfer constants were determined for several vinyl monomers using *N*-allylstearamide as the solvent. *N*-Allylstearamide was selected because its homopolymerization characteristics¹⁴ and copolymerization parameters¹⁵ were known, and because of its ease of preparation.¹⁶ Four vinyl monomers, namely, styrene, methyl methacrylate, vinyl acetate, and diethyl maleate, were chosen because of their large differences in reactivity in vinyl copolymerization. Each occupies one of the four quadrants of the Price-Alfrey *Q* and *e* map.¹⁷ Calculated^{15,18a} instant copolymer compositions and reactivity ratios for each system investigated (Fig. 1) illustrate the reactivity differences. Since *N*-allylstearamide melts at 85°C., all polymerizations were conducted at 90°C. A useful and general empirical expression was derived which provides an estimation of molecular weight of copolymers containing allylic comonomers based on knowledge of the reactivity ratios for the system and the molecular weight of one or two copolymers of known allylic content.

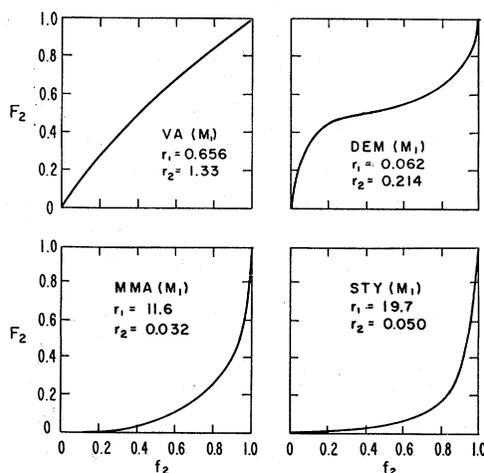


Fig. 1. Plots of mole fraction amide in the feed (f_2) vs. the initial mole fraction of amide in the copolymer (F_2) for vinyl acetate (VA), diethyl maleate (DEM), methyl methacrylate (MMA), and styrene (STY).

EXPERIMENTAL

Monomer Preparation and Purification

N-Allylstearamide was prepared from 99% pure methyl stearate. The amide was made in batches from 174 g. portions of ester. The reactions were run in crown-capped bottles at 70°C. for 24 hr. by using the procedure of experiment 2, previously described.¹⁶ The crude reaction product was isolated as in the reference procedure and crystallized from acetone (10 ml./g.) at 0°C. The yield was 80.69% of a product with m.p. 84.0–85.0°C.

ANAL. Calcd.: C, 77.95%; H, 12.77%; N, 4.33%. Found: C, 78.21%; H, 12.84%; N, 4.30%. The amide was 99% pure by gas-liquid chromatography.

All of the vinyl monomers were of the purest grades available commercially and were distilled before use, usually at reduced pressure, through an efficient column in a nitrogen atmosphere.

Copolymerization and Kinetic Procedure

N-Allylstearamide was charged by use of a long-stem funnel and weighed analytically into either a 25- or 50-ml. round-bottomed flask having a long neck (neck length 25.5 cm., I.D. 10 mm.). The vinyl monomer was introduced by use of a nitrogen-filled syringe fitted with a long needle and was weighed analytically. In general, 4 g. of vinyl monomers and 3–25 g. of *N*-allylstearamide were used for each series. The initiator, when used, was weighed into a small glass cup (length 15 mm., O.D. 9 mm.) and placed in the flask neck on a Teflon-coated bar magnet, held by a similar magnet strapped to the outside neck of the flask. The "elevator" so formed was lowered to the bottom of the neck, the flask was out-gassed five times at –80°C. and at reduced pressure, and sealed after filling with nitrogen. The elevator was then raised to the top of the neck while the amide was allowed to dissolve in the vinyl monomer at 90°C. At equilibrium, the outer bar magnet was removed, permitting the initiator cup to fall into the flask, thus initiating the polymerization. This time was noted as t_0 . During the solution and equilibrium period (30 min.) some thermal homopolymerization of styrene and methyl methacrylate occurred, but was experimentally determined to be negligible (<0.5% conversion). Some precipitation of polymer occurred with styrene and methyl methacrylate, but the vinyl acetate and diethyl maleate systems were homogeneous. Polymerizations were stopped at approximately 10% conversion in most instances (see Table I); the polymers were isolated by precipitation in excess hot methanol, extracted free of amide with hot methanol (except for vinyl acetate, with which petroleum ether, b.p. 63–70°C., was used), and were dried in a vacuum oven at 50°C. to constant weight. Rates were computed by assuming a linear relation for the conversion-time curve between t_0 and t . Quantities in grams were converted to moles per liter by determining, in separate experiments, density at 90°C. as a function of mole fraction for styrene, and methyl methacrylate, at

TABLE I
Molecular Weights and Compositions of the Copolymers

Experiment No.	\bar{M}_n	$1/\bar{X}_n \times 10^4$	$\frac{[S]}{[M]}$	Amide in	Amide in copolymer		Conversion, %	
				feed f_2	F_2	Found ^a	Homo-polymer ^b	Copolymer ^c
Styrene, no added initiator								
1	1,230,000	0.847	0	0	0	0	4.78	4.78
2	348,300	3.07	0.234	0.190	0.013	0.017	5.36	3.24
3	286,400	3.84	0.534	0.348	0.027	0.032	4.17	1.69
4	173,300	6.58	0.930	0.482	0.045	0.025	3.15	0.93
5	99,800	13.27	2.49	0.713	0.121	0.026	5.32	0.87
6	56,250	25.14	3.96	0.798	0.170		2.79	0.33
Styrene, initiated with benzoyl peroxide ^d								
7	128,200	8.12	0	0	0	0	12.24	12.24
8	100,000	10.74	0.250	0.200	0.015	0.020	12.81	7.44
9	74,850	14.79	0.537	0.349	0.030	0.030	12.26	5.07
10	71,500	16.10	0.981	0.495	0.050	0.046	14.52	4.17
11	51,200	24.84	2.16	0.684	0.105	0.041	9.78	1.73
12	34,700	40.11	3.69	0.787	0.160		5.14	0.66
Methyl methacrylate, initiated with benzoyl peroxide								
13 ^e	5,555,000	0.18	0	0	0	0	10.53	10.53
14	2,640,000	0.38	0	0	0	0	11.57	11.57
15	777,500	1.35	0.250	0.199	0.021	0.012	10.89	6.01
16 ^e	433,200	2.44	0.252	0.201	0.026	0.020	10.10	6.04
17	282,300	3.87	0.520	0.342	0.042	0.024	8.07	3.42
18 ^e	374,150	2.93	0.536	0.349	0.043	0.011	6.21	2.58
19	270,500	4.31	0.982	0.496	0.075	0.025	9.33	2.71
20 ^e	322,350	3.62	0.989	0.492	0.075	0.031	4.76	1.52
21	179,500	7.39	2.19	0.687	0.146	0.033	8.19	1.59
22 ^e	179,850	7.41	2.18	0.686	0.149	0.087	9.26	1.84
Vinyl acetate, initiated with benzoyl peroxide ^f								
23	244,500	3.52	0	0	0	0		14.95
24	53,600	17.49	0.022	0.021	0.032	0.020		11.59
25	32,600	30.74	0.042	0.040	0.060	0.034		11.01
26	24,500	43.60	0.063	0.060	0.087	0.046		10.92
27	21,150	54.20	0.086	0.079	0.121	0.060		10.93
28	17,050	69.00	0.102	0.093	0.133	0.079		18.58
Diethyl maleate, initiated with bisazoisobutyronitrile ^d								
29	9,875	248.3	0.344	0.256	0.482	0.403		2.42
30	9,430	262.8	0.495	0.331	0.500	0.405		3.76
31	9,605	260.4	0.658	0.397	0.515	0.393		4.23
32	9,390	269.6	0.993	0.498	0.535	0.440		4.42
33	9,325	273.9	1.34	0.573	0.550	0.454		3.69
34	8,995	287.9	1.87	0.651	0.573	0.433		3.23

^a From % nitrogen determinations on the copolymer.

^b Calculated as $[\text{g. polymer} - (\text{g. polymer} \times \text{weight fraction of amide in polymer})] \times 100/\text{initial weight of vinyl monomer}$.

^c Calculated as $\text{g. polymer}/\text{g. total monomer} \times 100$.

^d $[\text{Initiator}]/[\text{styrene}] = 3.50 \times 10^{-4}$; $[\text{initiator}]/[\text{diethyl maleate}] = 5.0 \times 10^{-3}$.

^e No added initiator.

^f Initiator amount necessary to yield 10% conversion calculated by use of constants of eq. (3).

several amide concentrations. Densities were read off of the smooth curve. During the density measurements, added hydroquinine (0.1 wt.-%) was experimentally determined to inhibit polymerization. Monomer and initiator (benzoyl peroxide) concentrations used for the vinyl acetate (Table I) experiments were $[VAc] = 10.82, 9.96, 9.20, 8.52, 7.91,$ and 7.36 mole/l. and $[I] = 0.196, 0.951, 2.19, 4.42, 7.35,$ and 18.96 mmole/l. for experiments 23, 24, 25, 26, 27, and 28, respectively. The rate of polymerization and $R_p/[M]^2$ for experiment 23 were 17.97×10^{-4} mole/l.-sec. and 15.34×10^{-6} l./mole-sec.; the rate of copolymerization and of $R_p/[M]^2$ for experiment 27 were 4.30×10^{-4} mole/l.-sec. and 5.82×10^{-6} l./mole-sec. The rate of copolymerization for experiment 32 of the diethyl maleate series was 0.14×10^{-4} mole/l.-sec. The comonomer concentration was 3.6 mole/l.

Solution Properties

Osmometric molecular weights were determined with a Mechrolab membrane osmometer, Model Number 501, and Schleicher and Schuell type 0-8 membranes. Duplicate determinations were made at 37°C. in toluene at four concentrations; when diffusion was noticed, extrapolation to zero time was attempted. The instrument was frequently checked on N.B.S. polystyrene #705, and only membranes yielding values within 3% of the standard were used.

Statistical Analysis

Regression coefficients, intercepts, and the mean deviation, s , of the regression coefficients for the data fitting eqs. (3), (4), and (5) were obtained on an IBM 1130 computer by using program designation IBM POLRG.

TABLE II
Mean Deviations at the Slopes

Monomer	Equation no.	$s \times 10^3$
Vinyl acetate	3	± 130
Styrene, thermal	4	± 0.037
Styrene, initiated	4	± 0.43
Methyl methacrylate	4	± 0.28
Diethyl maleate	4	± 0.32
Vinyl acetate	4	± 2.01
Styrene, thermal	5	± 1.3
Styrene, initiated	5	± 1.4
Vinyl acetate	5	± 0.28
Diethyl maleate	5	± 5.0

In all cases the data did not deviate significantly from a one degree polynomial, so that a linear regression was allowed. The mean deviations s at the slopes are listed in Table II.

RESULTS AND DISCUSSION

Experimental Results and Rate Data

Experimental results are listed in Table I. Because copolymerization occurred together with transfer, the table lists the monomer feed composition as mole fraction of amide f_2 , and the initial copolymer composition as mole fraction of amide in the copolymer F_2 , together with the *N*-allylamide to monomer mole ratio, $[S]/[M]$. Conversions reflect both vinyl monomer and comonomer disappearance. The amide content of the copolymers F_2 was computed from the reactivity ratios (Fig. 1), which were estimated from Q and e parameters determined for three copolymer systems.¹⁵

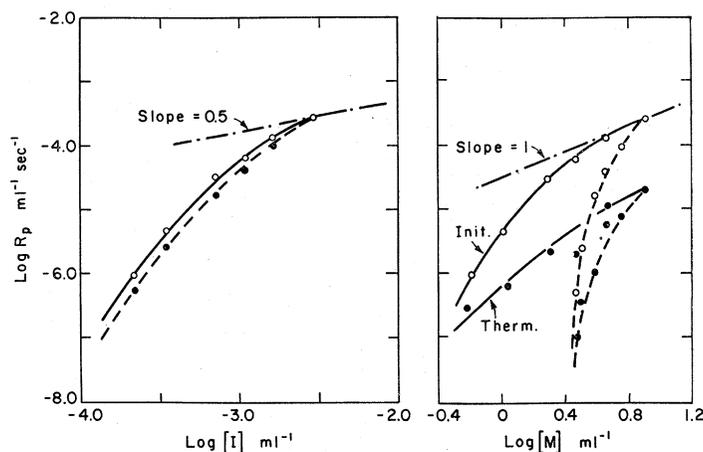


Fig. 2. Plots of $\log R_p$ vs. $\log [I]$ and $\log [M]$ for styrene polymerized in *N*-allylstearamide at 90°C.: (—) as rates of styrene homopolymerization in amide "solvent" and (---) as rate of styrene-amide copolymerization. Peroxide initiated (Init.) and thermally initiated (Therm.) data included. Allyl amide content increases from right to left.

These values were considered to be more reliable than the values found by nitrogen analysis (column 7, Table I) because of the very low nitrogen content of *N*-allylstearamide (4%) and its low incidence in some of the copolymers studied. In any case, the found value tended to support the calculated values, although they were generally lower. Molecular weights \bar{M}_n declined rapidly with increase in allylamide content, the effect being most pronounced with vinyl acetate. Relatively constant composition and low molecular weight were found for the diethyl maleate system regardless of feed composition.

Rate data are shown in Table III for both styrene and methyl methacrylate, with and without added initiator. Both homopolymerization and copolymerization rates are given. In these two systems, where little amide enters the copolymer even at high dilution, rates of homopolymerization might be expected to resemble rates in simple solvents. However, the ratio $R_p/[M]^2$ tended to rise and then fall to low values for homopolymer-

ization and to rapidly drop for copolymerization. This ratio, should be constant with dilution in thermal polymerization and in initiated polymerizations^{19a} when the initiator to monomer ratio is constant. It would appear that complex kinetics accompanied by marked rate retardation characterized these two systems.

In the absence of retardation, rates of vinyl homopolymerization are often proportional to the 0.5 power of the initiator concentration and to the first power of the monomer concentration:

$$R_p = K [I]^{0.5} \quad (1)$$

$$R_p = K' [M] \quad (2)$$

In Figure 2, $\log R_p$ for homopolymerization and copolymerization (Table III) is plotted as a function of $\log [I]$ and $\log [M]$ for the styrene system. As the concentration of *N*-allylstearamide increases, a continuous rise in the exponential dependence of both initiator and monomer concentration can be seen by comparison with the 0.5 and 1.0 power slope indicated in

TABLE III
Rates of Homopolymerization and Copolymerization for Styrene and Methyl Methacrylate in *N*-Allylstearamide at 90°C.

Experiment No.	Concentration, mole/l.		Initiator concn. $\times 10^3$, mole/l.	$R_p \times 10^4$, mole/l.-sec.		$R_p/[M]^2 \times 10^6$, l./mole-sec.	
	Vinyl monomer	Comonomer		Homopolymerization	Copolymerization	Homopolymerization	Copolymerization
Styrene, no added initiator							
1	8.09	8.09	0	0.215	0.215	0.328	0.328
2	4.64	5.73	"	0.126	0.094	0.584	0.286
3	2.99	4.60	"	0.020	0.078	0.225	0.368
4	2.04	3.95	"	0.021	0.012	0.504	0.077
5	0.91	3.17	"	0.0067	0.004	0.810	0.038
6	0.60	2.96	"	0.0031	0.001	0.870	0.012
Styrene, initiated with benzoyl peroxide							
7	8.09	8.09	2.87	2.75	2.75	4.20	4.20
8	4.51	5.63	1.61	1.38	1.00	6.78	3.16
9	2.99	4.59	1.07	0.661	0.420	7.40	1.99
10	1.96	3.89	0.701	0.309	0.176	8.03	1.16
11	1.03	3.25	0.348	0.046	0.026	4.34	0.246
12	0.64	2.99	0.215	0.009	0.005	2.20	0.056
Methyl methacrylate, initiated with benzoyl peroxide							
13 ^a	8.59	8.59	0	5.02	5.02	6.80	6.80
14	8.59	8.59	0.070	5.52	5.52	7.48	7.48
15	4.30	5.48	0.393	2.23	1.57	12.1	5.23
16 ^a	4.18	5.23	0	0.469	0.351	2.69	1.28
17	3.12	4.75	0.251	0.140	0.902	14.4	4.00
18 ^a	3.07	4.71	0	0.264	0.169	2.81	0.76
19	1.99	3.95	0.424	1.55	0.891	39.0	5.72
20 ^a	2.11	4.19	0	0.186	0.118	4.18	0.67

^a No added initiator.

the figure. In the methyl methacrylate system, initiator was varied somewhat, so that a similar comparison could not be made for the initiator concentration. Similar results, however, were obtained for the thermally initiated polymerization with respect to the monomer concentration. These data indicate that rates fall off rapidly as amide content increases. Both thermal and initiated data are moving toward very low rates as *N*-allylstearamide homopolymerization is approached with dilution. It would seem that degradative chain transfer is effectively controlling rate in these systems by removing active centers. However, a cross-termination effect^{19b} is not excluded. It is pertinent that rates of copolymerization of styrene and vinyl stearate were observed in this laboratory to be extremely low. Here degradative effects are excluded.

In contrast to the two previous copolymerizations, initiator consumption was very large in the vinyl acetate system, implying that rates were high because of induced peroxide decomposition.¹⁴ Actually, the limited rate data given in the experimental section for the vinyl acetate system indicate that the rates of copolymerization had been somewhat lowered. The derivative of monomer to peroxide consumption, dM/dP ,²⁰ declined rapidly as the amide concentration increased. The variation of dM/dP as a function of mole fraction of amide in the copolymer was observed to follow the empirical relation

$$dM/dP = (dM/dP)_{\text{amide}} (F_2)^{-a} \quad (3)$$

where F_2 is the mole fraction of amide entering the instant copolymer, $(dM/dP)_{\text{amide}}$ is the derivative for the *N*-allylstearamide homopolymer, and a is a constant. A plot of $\log dM/dP$ as a function of $\log F_2$ was linear (Fig. 3), yielding the parameter, $a = -1.89$, as the slope and $(dM/dP)_{\text{amide}} = 2.02$, as the intercept. dM/dP for the homopolymer had previously¹⁴ been found to be about 2.0, in close agreement with the extrapolated value of eq. (3). Use was made of eq. (3) to calculate the initiator needed to obtain a 10% conversion at reaction times exceeding the whole life of the peroxide (17 hr.). These initiator concentrations are given in the experimental section. The initiator dependence for diethyl maleate was much less than for vinyl acetate but was still considerable (Table I).

The difference in rates and in initiator dependence between styrene and methyl methacrylate on one hand, and between vinyl acetate and diethyl maleate on the other, is probably related to differences in vinyl monomer reactivity. The reactive monomers, styrene and methyl methacrylate, add radicals from the peroxide rapidly to initiate chains, while degradative chain transfer lowers both rates of copolymerization and the degree of polymerization. In contrast, the relatively unreactive monomer vinyl acetate is reluctant to add radicals, thus encouraging induced decomposition of the peroxide by amide "solvent" radicals.¹⁴ Although rates are apparently still lowered, considerable wastage of peroxide occurs. Hence, decreasing values of dM/dP were found as amide content was increased.

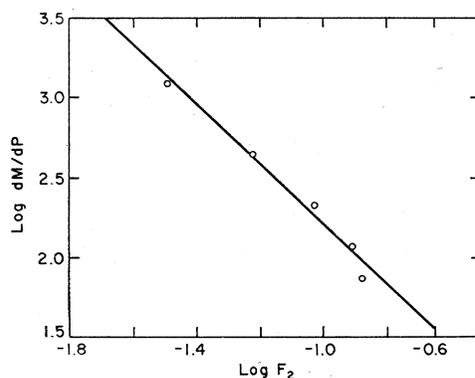


Fig. 3. Relation between $\log dM/dP$ and the log of the mole fraction of amide entering the copolymer (F_2) with vinyl acetate.

Induced peroxide decomposition and initiator wastage were particularly severe in the homopolymerization of *N*-allylstearamide.¹⁴ Results with diethyl maleate are a little surprising. Olefins 1,2-disubstituted by electron-withdrawing groups, when copolymerized with allylic monomers, characteristically display high rates and induced peroxide decomposition.⁴ Rates for the present system seem a little low on the basis of very limited data (see the Experimental section).

Determination of the Apparent Transfer Constants

Apparent transfer constants were determined for all four vinyl monomers by using the relation of Mayo:²¹

$$1/\bar{X}_n = 1/\bar{X}_{n_0} + C_S[S]/[M] \quad (4)$$

where $[S]$ is the *N*-allylstearamide concentration, $[M]$ the vinyl monomer concentration, \bar{X}_n the degree of copolymerization, \bar{X}_{n_0} the degree of polymerization of the vinyl comonomer, and C_S the transfer constant. Because of the variation found in $R_p/[M]^2$ and the marked lowering of rates already discussed, as well as the complications caused by the entrance of amide "solvent" into the polymer chain, values of C_S are considered to be only apparent values and are designated by primes. This follows a modification of the usage employed by Clark.¹⁰ A plot of $1/\bar{X}_n$ versus $[S]/[M]$ is shown in Figure 4 for all of the systems studied, and the regression coefficients and the intercepts are listed in Table IV. The transfer coefficients increased in the order: methyl methacrylate < styrene < diethyl maleate < vinyl acetate, which is the approximate order of decreasing monomer reactivity. This general order had previously been observed for monomers of similar reactivity.^{10,12,13} However diethyl maleate, which has nearly the same reactivity as vinyl acetate, has a much lower transfer constant. The lower slope together with the large extrapolated intercept found for this monomer (Fig. 4) are seen to reflect the small variation in copolymer composition caused by the alternation characteristic of ethylenes 1,2-disub-

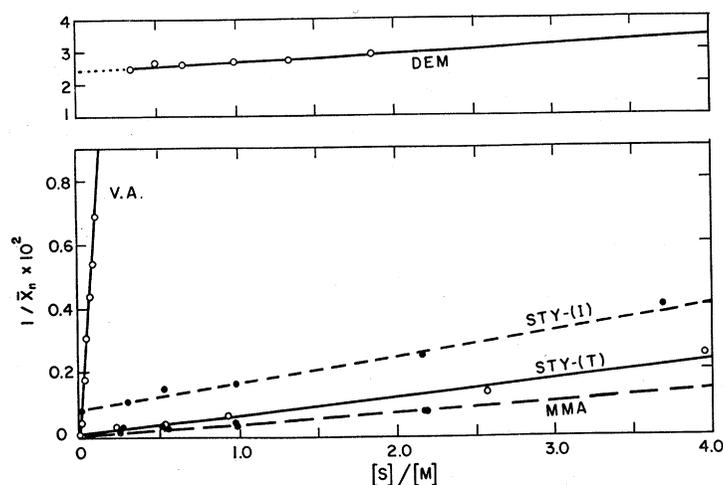


Fig. 4. Plots of $1/\bar{X}_n$ against $[S]/[M]$ for (MMA) methyl methacrylate, (STY-T) thermally polymerized styrene, (STY-I) styrene initiated by benzoyl peroxide, (VA) vinyl acetate, and (DEM) diethyl maleate in *N*-allylstearamide at 90°C.

stituted by electron-withdrawing groups when copolymerized with allyl monomers. Because C_M for diethyl maleate is unknown, the real curve for the relation between $1/\bar{X}_n$ and $[S]/[M]$ for 1,2-disubstituted olefins cannot be drawn. However, it is of interest that a literature value⁴ of \bar{X}_n for a 1:1 maleic anhydride-allyl acetate copolymer was 54, as determined in water, close enough to the value of 37 found in this work at the same composition to suggest a common relation for the two systems.

An increase was found in the value of C_S' for styrene initiated by benzoyl peroxide over the value obtained by thermal copolymerization (Table IV; Fig. 4). This is frequently observed in transfer studies.²² Corrections for initiated systems, such as used by Palit,²² could not be used here because of the variable dependence of rate on the monomer and initiator concentra-

TABLE IV
Regression Coefficients for Transfer of the Vinyl Monomers in
N-Allylstearamide at 90°C.^a

Comonomer	$C_S' \times 10^{3b}$	$(1/\bar{X}_{n0}) \times 10^{3c}$	$(1/\bar{X}_{n1}) \times 10^{3d}$	$K_1 \times 10^2$	$K_2 \times 10^2$
Styrene, no initiator	0.582	0.090	0.056	1.32	8.67
Styrene, peroxide initiated	0.830	0.857	0.768	1.91	8.01
Methyl methacrylate	0.301	0.101	0.074	0.46	9.53
Vinyl acetate	62.01	0.389	0.291	4.65	5.32
Diethyl maleate	2.24	24.6	6.28	3.89	5.48

^a Mean deviations of the slopes are listed in Table II.

^b The degree of polymerization (\bar{X}_n) estimated from the copolymer composition based on F_2 of Table I.

^c Intercept of the Mayo equation, eq. (4).

^d Intercept of eq. (5).

tion. In contrast, the methyl methacrylate data were apparently insensitive to initiator concentration because the regression line fitted both the thermal and initiated experiments equally well.

Although increasing and rather substantial amounts of initiator (see the experimental section) had to be used in the vinyl acetate copolymerization to obtain a 10% conversion, curvature was not observed in the transfer regression line (Fig. 4). It appears that chain transfer in this instance terminates all chains because chain length was dependent on the amide concentration only, and was independent of initiator concentration. This resembles allylic homopolymerization,^{1,20} where \bar{X}_n is independent of initiator concentration.

Estimation of the Degree of Polymerization of Allylic Copolymers

When the reciprocal number-average degree of polymerization ($1/\bar{X}_n$, Table I) was plotted as a function of the mole fraction of amide entering the copolymer F_2 for all five systems, the relation was found to be linear:

$$1/\bar{X}_n = 1/\bar{X}_{n1} + K_1 F_2 \quad (5)$$

where $1/\bar{X}_{n1}$ is the reciprocal degree of polymerization for the vinyl comonomer $1/\bar{X}_{n0}$ of the Mayo equation, eq. (4), and K_1 is a constant. This equation is therefore related to the copolymerization equation, since

$$F_2 = 1 - F_1 = 1 - (r_1 f_1^2 + f_1 f_2)/(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \quad (6)$$

When eq. (5) was extrapolated to the limit $F_2 = 1$, the reciprocal number-average degree of polymerization for *N*-allylstearamide ($1/\bar{X}_{n2} = 0.1$) was not obtained in any experiment.¹⁴ Values were always considerably less than the true value and varied with the vinyl monomer. An empirical equation was derived which extended the relationship of eq. (5) to the limit of unity in F_2 . This was done by adding a term of higher degree in F_2 modified by a coefficient representing the difference between the value of the linear regression through F_2 , $(1/\bar{X}_{n2} - 1/\bar{X}_{n1})$, and the experimental value of K_1 , to give

$$1/\bar{X}_n = 1/\bar{X}_{n1} + K_1 F_2 + K_2 (F_2)^3 \quad (7)$$

where K_1 and $1/\bar{X}_{n1}$ are the coefficient and intercept, respectively, of eq. (5) and $K_2 = [(1/\bar{X}_{n2}) - (1/\bar{X}_{n1})] - K_1$. The regression coefficients for K_1 and values of K_2 and $1/\bar{X}_{n1}$ are given in Table IV for all five systems, while the mean deviations are given in Table II. Plots of eq. (7) for three of the systems studied are shown in Figure 5. The solid lines representing the experimental slopes, K_1 of eq. (5), are extended beyond the experimentally determined portion of the abscissa F_2 , to clarify the calculated curves. The dashed lines define the calculated curves and can be seen to fit the experimental data fairly well. The curvature required by eq. (7) was fixed by the available experimental data; terms of higher degree in F_2 would, of course, lower the slope. Because data were not available at higher values of F_2 to more clearly define the

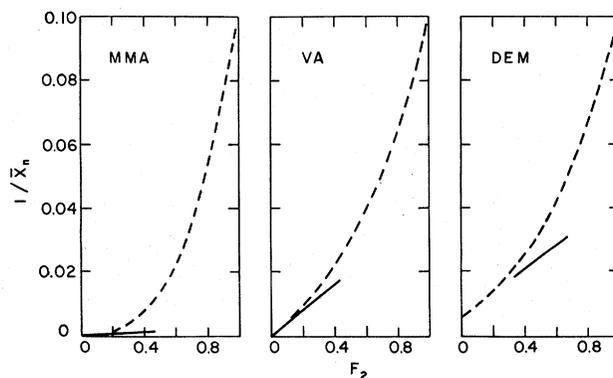


Fig. 5. Empirical relation between $1/\bar{X}_n$ and F_2 [eq. (7)], dashed line, compared with the initial slope [K_1 of eq. (5)] for (MMA) methyl methacrylate, (VA) vinyl acetate, and (DEM) diethyl maleate in *N*-allylstearamide at 90°C.

curvature, eq. (7) represents an upper limit for the rate of decrease in molecular weight resulting from allylic copolymerization. The intercepts $1/\bar{X}_{n1}$ and $1/\bar{X}_{n0}$ (Table IV) are significantly different, suggesting that curvature actually present in eq. (5) distorted the fitted linear regression line and

TABLE V
Transfer Constants from the Literature for Vinyl Monomers in Allyl Monomers

Vinyl monomer	Allylic monomer	Polymerization temp., °C.	$C'_s \times 10^3$	$(1/\bar{X}_n) \times 10^3$	$K_1 \times 10^2$	$K_2 \times 10^{2a}$	Reference
Styrene	Allyl chloride		1.51 ^b	0.75	5.45	6.07	2
Ethyl acrylate	Allyl chloride	30	0.15 ^b	0.05	0.37	11.23	5
Acrylonitrile	Allyl alcohol	30	0.595 ^b	0.15 ^c	0.16	19.82	3
Vinyl acetate	Allyl chloride	60	310.0	0.25 ^c	15.1	-3.54	10
Vinyl acetate	Allyl acetate	60	90.0	0.25 ^c	12.7	-7.73	10
Vinyl acetate	Methallyl chloride	60	40.0	0.25 ^c	1.50	8.48	10
Styrene	<i>n</i> -Hexene-1	60	0.25	0.25 ^b	0.76	9.22	13
Methyl methacrylate	<i>n</i> -Butene-1		0.51	0.10 ^d	1.58	8.40	12

^a $1/\bar{X}_{n2}$ of allyl chloride = 0.116²⁶; of allyl alcohol = 0.2³; of allyl acetate = 0.05²⁰; for other monomers, a value of 0.1 was assigned.

^b Estimated from the experimental data given in the reference.

^c $C_M = 1/\bar{X}_{n1}$ assumed from the reference data.

^d Assumed to be the same as $1/\bar{X}_{n0}$ of Table IV.

caused a lowering of the intercept, $1/\bar{X}_{n1}$. The parabola expressed by eq. (7) probably does not describe the true slope of the theoretical curve for the diethyl maleate systems. This might be expected to be sigmoidal for $0 < F_2 < 1.0$ in analogy with the slope of the instant copolymer-composition curve (Fig. 1). However, because only copolymers between $F_2 = 0.4$ and 0.6 can usually be made with olefins 1,2-disubstituted by electron-withdrawing groups, the parabolic expression comes fairly close to predicting experimental values even in this limiting case.

Literature data were used to estimate the parameters C'_S , K_1 , K_2 , and $1/\bar{X}_{n1}$ for several vinyl monomers copolymerized with various allylic comonomers. Data are shown in Table V. The parameters K_1 were calculated from given values of C_S and $1/\bar{X}_{n1}$ and low values of F_2 (< 0.1). Allylic content F_2 was computed from reactivity ratios derived from the respective Q and e parameters.^{18a} When C_S was not available, this constant was estimated from \bar{X}_n taken from experimental intrinsic viscosities (by using an appropriate Mark-Houwink relation^{18b}) and the polymer-composition data provided in the paper. While these can be considered to be only rough estimates, the agreement with the data in Table IV is fairly good, if the parameters for vinyl monomers of similar reactivity are compared. When transfer constants are particularly large, K_1 exceeds $[(1/\bar{X}_{n2}) - (1/\bar{X}_{n1})]$, and K_2 is then negative. This occurred for allyl acetate and allyl chloride in this series.

Equation (7) can be used for estimating the molecular weight of an allylic copolymer, when the reactivity ratios and C_{M1} and C_{M2} are known and when molecular weights of one or two copolymers of low allylic content are available. Because the copolymerization equation [eq. (6)] holds only for chains of fairly high degree of polymerization,²³ both this equation [and eq. (7)] may fail at high F_2 , where the degree of polymerization is low. Mixtures containing homo-oligomers might result from attempts at copolymerization, especially where monomer reactivity differences are great.

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