Intrinsic Viscosity-Number Average Molecular Weight Relationship for poly(n-Octadecyl Acrylate) and poly(N-n-Octadecylacrylamide)[1]

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Abstract

Intrinsic viscosity-number average molecular weight relationships have been measured, at 30C in benzene, for poly(n-octadecyl acrylate) as $[\eta] = 2.72 \times 10^{-4}\ M_n^{0.638}$ and for poly(N-n-octadecylacrylamide) as $[\eta] = 0.82 \times 10^{-4}\ M_n^{0.676}$. Whole polymers of various molecular weights were prepared in benzene solution at 65C with dodecyl mercaptan as primary regulator. By the use of these parameters, the molecular weight of such polymers and their homologs may now be measured by simple solution-viscosity determinations.

In the expression $1/\overline{X}_n = 1/\overline{X}_{no} + C_S[S]/[M]$ (relating degrees of polymerization $\overline{X}_n$ to the mercaptan/monomer ratio), intercept $1/\overline{X}_{no}$ and apparent transfer constant C_S for n-octadecyl acrylate were 6.28×10^{-3} and 0.68; for N-n-octadecylacrylamide 1.10×10^{-3} and 0.62 respectively. These parameters permit preparation of homopolymers of chosen molecular weight.

Introduction

There is a simple empirical relationship between the intrinsic viscosity of a polymer and its molecular weight, measured by an absolute method. In the equation

$$[\eta] = K'M^a \qquad (1)$$

$[\eta]$ is defined as the limiting viscosity number, M as the molecular weight and K′ and a are constants. Molecular weight may be number-average ($\overline{M}_n$), which represents the average of the number of polymer chains, or weight-average ($\overline{M}_w$), which emphasizes their relative size. The difference in the two absolute methods, applied to the same system, resides in small differences in the values of K′; the values of a are usually the same. Experimentally, values of intrinsic viscosity and molecular weight, on either whole polymers or on fractions are used to evaluate K′ and a for a specific solvent at a selected temperature. Although whole polymers are often used for evaluation, fractionated polymers of relatively narrow distribution are employed for the most precise results. If whole polymers are used for this purpose, samples are prepared under conditions which vary the chain length while keeping the molecular-weight distribution as narrow as possible. Practical advantage of the relationship results from the greater experimental ease of determining intrinsic viscosity compared to either number- or weight-average molecular weight. Thus, by the use of the constants, molecular weights of a polymer may be estimated from simple determination of solution viscosities within the range covered by the relationship. Numerical values of the parameters are of theoretical interest in estimating the extensibility of the polymer molecule in the solvent. Constants, related to the thermodynamics of polymer solutions, are obtained as the slopes of the relations between polymer concentration and the characteristics ordinates used for the determination of intrinsic viscosity, and, respectively, number- and weight-average molecular weight.

It appears that the only intrinsic viscosity-number average molecular weight relationship previously determined for a long-chain homopolymer was obtained for poly-n-nonyl methacrylate in benzene (1), although weight-average molecular weight relations have been measured for many n-alkyl methacrylate homologs (2–9). Number-average relationships for n-alkyl acrylate homologs have been limited to whole polymers of methyl acrylate in acetone at 30C (10), and in benzene at 35C (11), and to whole and fractionated polymers of ethyl acrylate at 30C in a variety of solvents (12,13). Weight-average relations were available on only two acrylamides, poly-N-n-dimethylacrylamide (14) and poly-N-tert-butylacrylamide (15).

In this study the relationship between intrinsic viscosity and number-average molecular weight was determined for two long-chain vinyl polymers of related structure, poly-n-octadecyl acrylate and poly-N-n-octadecylacrylamide. Whole polymers, carried to high conversions, were employed to afford data under representative preparative conditions. All polymerizations were conducted in benzene at 65C. Molecular weight was controlled by the combined effects of chain-radical termination, transfer to solvent, and transfer to n-dodecyl mercaptan. By keeping the benzene-monomer ratio constant while varying mercaptan, apparent transfer constants were obtained for the interaction of each monomer radical with this thiol. Because the transfer constants approached unity for each monomer, indicating equal rates of disappearance of monomer and thiol, it seemed reasonable to expect fairly narrow molecular-weight ranges, conforming to the most probable distribution (16) for the two polymers when termination was by transfer.

Experimental

Preparation of Monomers

A supply of n-octadecyl acrylate was obtained under special purchase from Monomer-Polymer Corporation and its physical properties have been described (17); the preparation and purification of N-n-octadecylacrylamide has also been described (18). The amide and ester were respectively 98.5% and 95% pure by gas-liquid chromatography. The ester was 99% pure by ester number; its impurities appeared to be the lower homologs.

Polymerization Procedure

Approximately 0.040 moles of each monomer in 0.338 moles of benzene were heated under nitrogen in a sealed bottle, in a bath thermostatted at 65 ±

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0.1C for 24 hr, with various amounts of n-dodecyl mercaptan (see Table I) used as the primary regulator. Variation of the initiator (Table I) was also used to control molecular weight. The n-dodecyl mercaptan was made up as a stock solution in benzene (0.010 moles mercaptan per mole of acrylate ester; 0.01185 moles of mercaptan per mole of amide when used without further dilution) and was then diluted as required (Table I). The homopolymers were isolated by precipitation with methanol and freed of monomer by four extractions with methanol (10 ml/g polymer) at reflux. Polymerization data is shown in Table I.

Viscosity Measurements

In Ostwald-Fenske viscometers having flow times of about 240 sec, viscosity measurements were made at 30 ± 0.01C on solutions in A.C.S. benzene, previously distilled through a 2-ft helix column. Concentrations were in the range of 1 g per 100 ml and are expressed by g dl^{-1}. Shear effects were assumed to be negligible, and therefore no shear corrections were applied to the data. From the flow time of the polymer solution, t, compared to that of the solvent, t_o, specific viscosity η_{sp} was obtained for each concentration in accordance with the viscosity definitions:

$$\text{RELATIVE VISCOSITY} = \eta_r = \eta/\eta_0 \simeq t/t_0 \quad (2)$$

$$\text{SPECIFIC VISCOSITY} = \eta_{sp} = \eta_r - 1 \quad (3)$$

Dynamic Osmometric Molecular Weight Determinations

Dynamic osmometric molecular weights were obtained using a Mechrolab High-Speed Membrane Osmometer Model 501, at 37C in distilled toluene, using concentrations of 7 g of polymer per liter or less, depending on the molecular weight. The dynamics of each molecular weight determination was monitored on a Texas Instrument Servo-riter Recorder, Model P.W.S. The highest density Schleicher and Schuell membranes, types 0–8, were used. Equilibrium times were established to be 10 min for each concentration, and typically four concentrations were used for a determination. The instrument was checked on N.B.S. polystyrene #705, in sextuplicate using toluene as the solvent. The N.B.S. value was 172,000; that of this laboratory 177,000 ± 1.24%. The difference was, therefore, 3%. The instrument was also checked against N.B.S. polystyrene whenever the membrane was changed or adjustments were made, a similar value being each time obtained. Each molecular weight determination was done in duplicate; where diffusion was noticed, in the polyoctadecyl acrylate series, up to six replications were performed, and extrapolations in severe cases were made to zero time. For the evaluation of A_2 and Γ, concentration was in g/ml; otherwise all concentrations were in g/liter.

TABLE I

Reaction Conditions and Percentage Conversion for the Preparation of the Homopolymers[a]

Sample number	Benzoyl peroxide, mole %	[S]/[M] $\times 10^3$[b]	Time, hr	Conversion, %
n-Octadecyl acrylate				
1	0.05	0	1.75	14.8
2	0.05	0	2.58	33.6
3	0.25	0	24.0	92.5
4	0.25	0.25	24.0	94.5
5	0.25	0.50	24.0	94.0
6	0.50	2.50	24.0	95.7
7	1.00	10.00	24.0	90.9
N-n-Octadecylacrylamide				
1	0.25	0	0.67	66.9
2	0.05	0	1.33	12.4
3	0.25	0	24.0	95.9
4	0.50	0.60	24.0	97.4
5	0.75	2.95	24.0	97.9
6	1.00	11.85	24.0	75.2

[a] All samples polymerized in benzene (8.44 moles/mole of monomer) at 65C.

[b] [S] designates moles of dodecyl mercaptan; [M], moles of monomer.

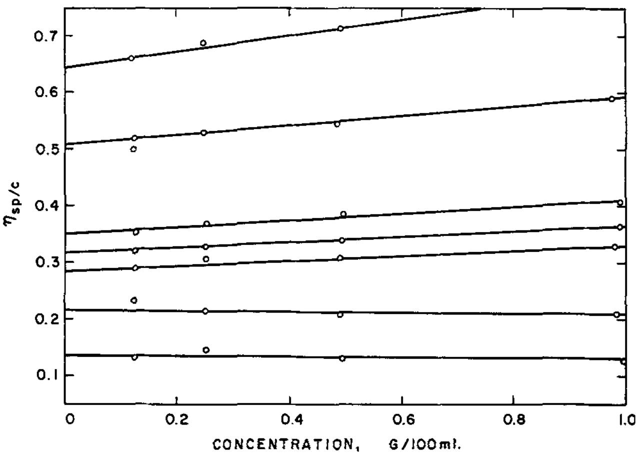

FIG. 1. Plot of η_{sp}/c versus concentration for poly-n-octadecyl acrylate in benzene at 30C.

Results and Discussion

Results of Viscometry and Osmometry

Intrinsic viscosities were obtained using the relation between specific viscosity and polymer concentration.

$$\eta_{sp} = [\eta] + k'[\eta]^2c \quad (4)$$

where intrinsic viscosity, $[\eta]$, was obtained as the intercept of the linear relation found when specific viscosity, η_{sp}, was plotted as a function of concentration, c. From the slope $k'[\eta]^2$, the Huggins constant k′ was evaluated. These data are illustrated for each monomer in Figures 1 and 2 and are listed for both polymers in Table II. Values of intrinsic viscosity were in the rather narrow range of 0.11 to 0.64 for both polymers studied. Considerable variation was also found in the polymer-solvent interaction parameter, k′. Deviations, usually positive, can be observed from the values of between 0.35 to 0.40 often found for this constant. These tended to occur in lower range of $[\eta]$ ($\leqslant 0.3$) where insensitivity in determining the low value of the slope (Fig 1,2) increases as values of $[\eta]^2$ become quite small, the combined effect increasing the value k′. This tendency can be observed in other systems (13).

Osmotic molecular weights were determined using the relationship between osmotic pressure, π, and concentration, c:

$$\pi/cRT = (A_1 + A_2c + A_3c^2 + \ldots\ldots) \quad (5)$$

$$\pi/cRT = 1/\bar{M}_n(1 + \Gamma c + g\Gamma^2c^2 + \ldots\ldots) \quad (6)$$

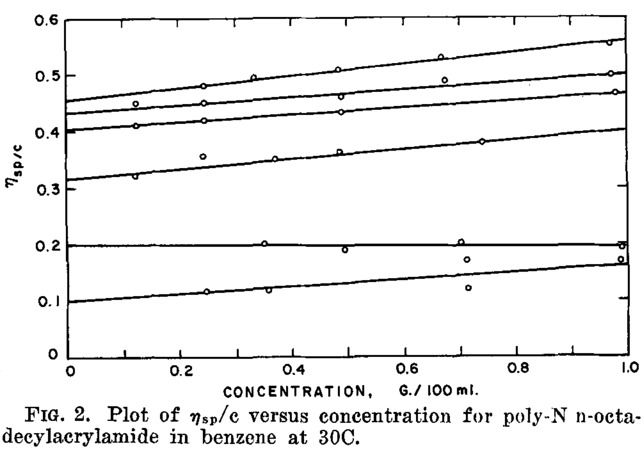

FIG. 2. Plot of η_{sp}/c versus concentration for poly-N n-octadecylacrylamide in benzene at 30C.

TABLE II
Solution Property Data for Whole Polymers of n-Octadecyl Acrylate and N-n-Octadecylacrylamide[a]

Sample number	Viscosity data at 30C		Osmometric data at 37C average values					
	$[\eta]$ dl g^{-1}	k′	$\overline{M}_n$	$\overline{X}_n$	Number of determinations	Deviation, %	$A_2 \times 10^4$ cm^3 mole g^{-2}	Γ cm^3 mole g^{-1}
poly-n-octadecyl acrylate								
1	0.643	0.334	196,900	607	3	3.08	2.67	52.6
2	0.510	0.338	171,900	530	2	3.66	2.03	35.0
3	0.350	0.571	55,000	169	2	3.09	5.57	30.6
4	0.318	0.495	54,000	166	2	1.85	4.81	26.0
5	0.282	0.629	45,800	141	4	2.35	3.45	15.8
6	0.218	0.526	38,400	118	6	1.09	4.82	18.5
7	0.138	1.05	25,100	77	6	4.51	9.50	23.8
poly-N-n-octadecylacrylamide								
1	0.457	0.503	338,500	1046	2	0.44	1.35	45.7
2	0.407	0.356	317,500	981	2	0.47	0.38	12.1
3	0.433	0.355	295,500	913	2	3.41	1.25	36.9
4	0.317	1.07	198,500	614	2	3.27	2.39	47.4
5	0.200	0	107,800	333	2	3.01	3.49	37.6
6	0.105	5.26	38,400	119	2	1.08	11.95	45.9

[a] Viscosity data obtained in benzene at 30C; osmometric data in toluene at 37C.

where A_1 = the intercept = $1/\overline{M}_n$, A_2 is the slope and A_3 is the coefficient of the next higher term in the expansion. Similarly, in the next expression $\Gamma = A_2/A_1$, Γ^2 is a higher term and g is a factor approximately equal to 0.25 in good solvents. In both expressions, R is the gas constant and T is the temperature in degrees Kelvin. A_2 and Γ are two forms of constants which reflect solvent-polymer interactions and are of interest as experimentally determinable expressions in polymer solution thermodynamics. The higher the value of either parameter the better the solvent. By use of low concentrations of polymer (< 8 g/l), the upward curvature, expressed by A_3c^2 and Γ^2c^2, was avoided. Plots of π/cRT against c are shown in Fig 3 and 4 for both monomers. Numerical values for $\overline{M}_n$, A_2, and Γ are shown in Table II. The molecular weight data shows the expected decline with decrease in $[\eta]$. The slopes, A_2, show a gradual decrease as $\overline{M}_n$ increases in accordance with predictions from the theory of polymer solution thermodynamics (19). Considerable variation in A_2 (Fig 3 and 4) was found, however, for the replicate runs of each experiment in the Table, for which the listed value is an average. Variation was of the order of ±17%. Some of this is reflected in the deviation from smooth progression seen in individual experiments in Table II. It was not known whether this variation was a result of factors inherently present in dynamic osmometry, which is a relatively unexplored technique compared to classic static osmometry, or whether the problem was an experimental one. However, the values of Γ were of the same order of magnitude as those found in a most careful study of the solution properties of polymethyl methacrylate (20), using static osmometry. The values of *a* for the polymethyl methacrylate and for the homopolymers reported in this paper were similar, indicating that good solvents were used in both cases. Thus, somewhat similar values for Γ are predicted. Of course, variation can be seen in values of Γ in Table II since it was derived from A_2. Because of these difficulties, values for these two parameters are only approximate. Further experimentation is required, perhaps using more monodisperse polymers, to elucidate the causes of this erratic behavior.

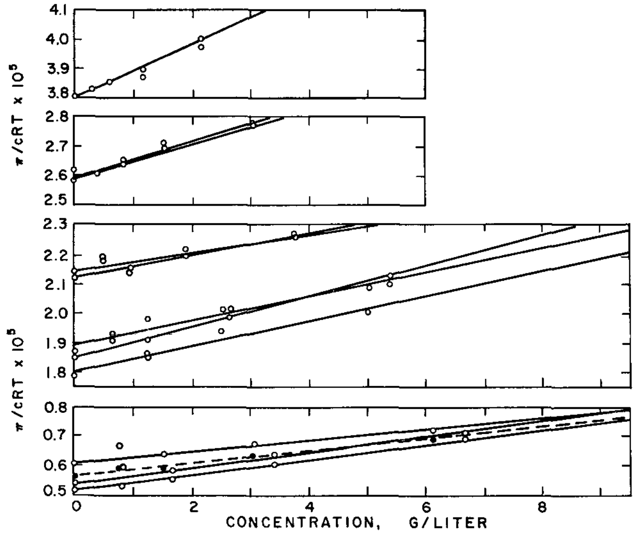

FIG. 3. Plot of π/cRT versus concentration for poly-n-octadecyl acrylate in toluene at 37C.

The Intrinsic Viscosity-Molecular Weight Relation

Plots of log $[\eta]$ against log $\overline{M}_n$ are shown in Fig. 5 for both homopolymers. From the slope and intercept respectively, *a* and K′ were estimated by regression analysis. The values of the parameters together with their 95% confidence limits are listed in Table III. Values of *a* usually fall between 0.5 and 1.0 for most polymers. An increase in the magnitude of the value toward 1 with change in solvent indicates increased polymer-solvent interactions (i.e., a progression toward a "good solvent"). The data found thus indicates a considerable and similar expansion of both polymer molecules in benzene from their unperturbed dimensions.

It is of interest that the values of *a* for poly-n-

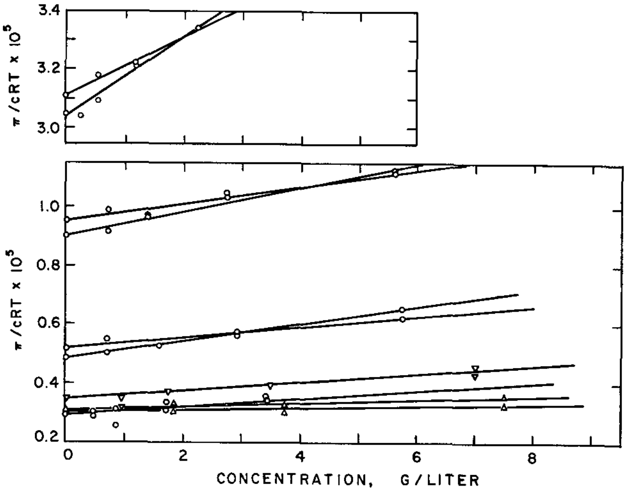

FIG. 4. Plot of π/cRT versus concentration for poly-N-n-octadecylacrylamide in toluene at 37C.

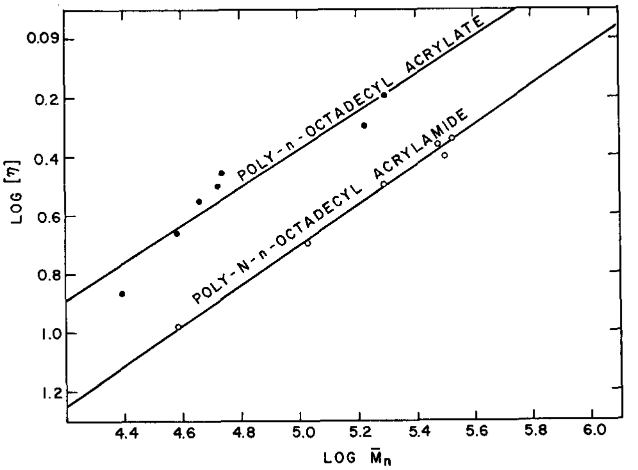

FIG. 5. Plot of log [η] versus log $\overline{M}_n$ for poly n-octadecyl acrylate and poly-N-n-octadecylacrylamide in benzene at 30C.

nonyl methacrylate in benzene at 35C was 0.65 and that of K′ was 1.48×10^{-4} (1). The similarity of the values of *a* for these three C_{18} polymers suggests that many long-chain vinyl monomers of different structure may have values of *a* close to 0.65 in benzene. However, differences in the value of K′ indicate that a relationship characteristic of one polymer structure will not apply to others.

With respect to homologs, however, there is some data available indicating general applicability. Chinai et al (2–5,21) have found the following values for the parameters of the poly-n-alkyl methacrylates in methyl ethyl ketone at 23–25C, in weight-average relationship: in the order $K' \times 10^4$, *a;* methyl 0.71, 0.72; ethyl 0.28, 0.79; n-butyl 0.16, 0.81; 2-ethylbutyl 0.22, 0.77; hexyl 0.21, 0.78. Thus, on the basis of this limited quantity of data, the application of the values in Table III to other polyacrylate or polyacrylamide homologs and homolog mixtures would not be in serious error.

The considerable scattering present in the poly-n-octadecyl acrylate system compared to the N-n-octadecylacrylamide is not understood. Because both polymers were prepared under very similar kinetic conditions, variations in molecular-weight distribution for individual polymers seems unlikely. Various degrees of branching through transfer to polymer occurring in the acrylate system only may account for the observation. Because the instrinsic viscosity of branched polymers is lower than the intrinsic viscosity of linear polymers of the same molecular weight (22), perturbations in the data might be caused by this phenomenon occurring to different degrees in individual experiments. However, the much greater opportunities for transfer to solvent and mercaptan in both systems renders this argument somewhat unconvincing. Of greater importance is the possibility of error caused by membrane permeation. Permeation was noticeable in the acrylate but not in the amide series. While the special advantage of dynamic osmometry lies in obtaining the osmotic pressure rapidly before appreciable permeation occurs (23), quantitative correction of osmotic pressure data for the presence of permeation has been shown to be theoretically impossible (24). Adjusting the data points at the left hand side of Figure 5 (where experimentally permeation was observed), by making the reasonable assumption that permeation was proportional to decrease in molecular weight, would have the effect of eliminating the observed scatter.

TABLE III

Parameters for the Relationship Between Intrinsic Viscosity and Number Average Molecular Weight for Whole Polymers in Benzene at 30C

Homopolymer	*a*	$K' \times 10^4$	log K′	$t_{05}S$	
				a	log K′
n-Octadecyl acrylate	0.638	2.72	−3.5672	±0.229	±1.105
N-n-Octadecyl-acrylamide	0.676	0.824	−4.0837	±0.066	±1.091

The relationships of Table III are probably only valid within the experimental range described. This is especially true of the lower range of molecular weight. It often happens that at a sufficiently low value of $\overline{M}_n$ a discontinuity develops, *a* drops to a lower value (usually 0.5) thus changing the value of K′. This has been observed for polymethyl methacrylate (20) and polyethylene (25).

The Apparent Transfer Constant to n-Dodecyl Mercaptan

The experimental data permitted an estimation of the apparent transfer constant for both monomer radicals toward n-dodecyl mercaptan using the relation of Mayo, given below in the generalized form described by Flory (26), in which all termination modes are considered:

$$1/\overline{X}_n = C_M + (k_t/k_p{}^2)R_p/[M]^2 + C_S[S]/[M] + C_I(k_t/k_p{}^2fk_d)R_p{}^2/[M]^3 \qquad (7)$$

In this, $\overline{X}_n$ = the degree of polymerization; C_M = the constant for transfer to monomer M; $C_S = k_{trS}/k_p$ = the constant for transfer to solvent S; $C_I = k_{trI}/k_p$ = the constant for transfer to initiator; k_p, k_t, and fk_d are specific rate constants for propagation, termination and initiation, respectively; and R_p is the rate of polymerization. The second term is the expression for chain combination. By holding the second term constant (i.e., making $R_p/[M]^2$ a constant) and keeping the last term vanishingly small by using a minimum amount of initiator, plots of $1/\overline{X}_n$ against the solvent-monomer ratio [S]/[M] will yield the constant for transfer to solvent, C_S, as the slope, and the sum of the first two terms as the intercept, $1/\overline{X}_{no}$. Adding a term to the intercept in equation (7) for transfer to benzene $C_S'[B]/[M]$, which is constant in the present case because [B]/[M] for both sets of data was kept constant at 8.44 (Table I), the expression becomes

$$1/\overline{X}_n = C_M + (k_t/k_p{}^2)R_p/[M]^2 + C_S'[B]/[M] + C_S[S]/[M] + C_I(k_t/k_p{}^2fk_d)R_p{}^2/[M]^3 \qquad (8)$$

Transfer to polymer was assumed to be small and was neglected as was the effect of diminishing monomer concentration on the overall relation. If large, both effects would raise the apparent transfer constant and produce variability in the data, proportional to the % conversion.

Plots of $1/\overline{X}_n$ against [S]/[M], designated the mercaptan to monomer ratio (Table I), are shown in Figure 6. The data can be seen to be reasonably linear, even though the ratio of initiator to monomer was not constant, as is required to keep $R_p/[M]^2$ constant. Errors caused by transfer to polymer and monomer depletion also seem small relative to the very large effect of transfer to mercaptan. The apparent transfer constants, estimated by regression analysis of the slopes in the figures, are given in Table IV, together with the value of the intercept, $1/\overline{X}_{no}$, which was considered to be the sum of the first three terms of equation (8). The observed transfer constants are designated "apparent" in this work to differentiate them from the body of values reported in the literature in which a more complete control of the kinetic variables was undertaken.

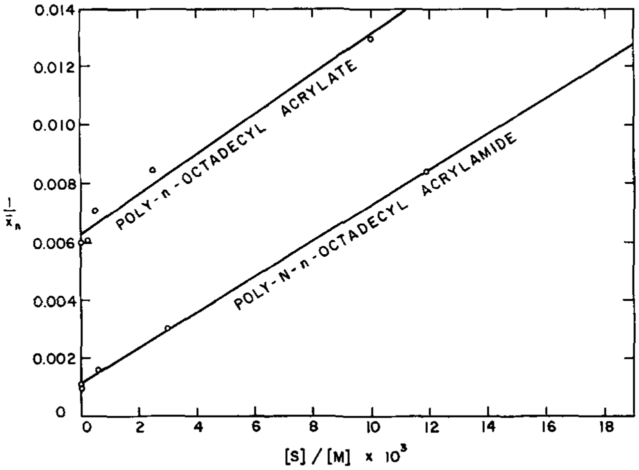

FIG. 6. Determination of apparent transfer constants at 65C for the monomers toward n-dodecyl mercaptan.

As can be seen, the values of C_S for both monomers were very similar, indicating somewhat the same reactivity for each of the two octadecyl radicals toward this thiol. On the other hand, a value of C_S for methyl acrylate toward n-butyl mercaptan at 60C was found to be 1.7 (27), while the value for n-octadecyl acrylate, in Table IV, was 0.68. Because n-butyl mercaptan behaves very similarily to n-dodecyl mercaptan toward like radicals, the reason for the discrepancy between the two homologs is not understood. It might be that a small difference in radical reactivities, accruing for every added methylene across the homologous series, might cause this difference. An analogous situation has been noted for differences observed between transfer to monomer for vinyl ester homologs, and transfer to ethyl esters of the same chain length by vinyl acetate (28). In this instance, also, the difference in transfer constants was by a factor of about 2.

Differences in the value of the intercept $1/\bar{X}_{on}$ indicate that the miscellaneous transfer processes of the ester polymerization exceeded in magnitude those of the amide; complexity of the quantity

$$1/\bar{X}_{no} = C_M + (k_t/k_p{}^2)R_p/[M]^2 + C_S{}'[B]/[M] \qquad (9)$$

prevents comparison by class of transfer. The apparent transfer constants C_S reported here are by their nature approximations, since initiator to monomer ratio was not held constant and there were no doubt errors arising from transfer to polymer and from monomer depletion under the high conversions employed.

TABLE IV

Apparent Transfer Constants for the Monomers Toward n-Docecyl Mercaptan at 65C

Homopolymer	Transfer parameters		$t_{05}S$	
	Cs	$1/\bar{X}_{no}$	Cs	$1/\bar{X}_{no}$
n-Octadecyl acrylate	0.682	0.00628	±0.193	±0.0016
N-n-Octadecylacrylamide	0.619	0.00110	±0.032	±0.00016

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