

SOLID AND LIQUID SOLUTION SCINTILLATORS CONTAINING  
MONOISOPROPYLBIPHENYL

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We have recently investigated the use of monoisopropylbiphenyl (MIPB) in the preparation of plastic scintillators which show pulse shape discrimination (1), and for liquid scintillators which are particularly suitable for direct counting on filter paper. A further investigation of the role of this solvent appeared desirable in order to elucidate the mechanism by which this compound affected the scintillation process and thereby made possible a differentiation in detection between light and heavy ionizing particles in the plastic scintillator. Similarly, observation of the low quenching action exhibited in liquid scintillators employing MIPB as solvent, prompted an investigation of the kinetics of quenching in such liquid scintillation systems. Although the behavior in liquid and plastic scintillators is probably not directly related, the results are nevertheless being combined in this report on the scintillation properties of MIPB.

PLASTIC SCINTILLATORS

We at first assumed that MIPB acted as a high boiling solvent or plasticizer in plastic scintillators. One would thus postulate that the polymer chains were merely diluted and to some extent disentangled by the presence of this solvent, and that energy transfer would take place through the combined aromatic medium. However, such a postulate requires the molecular weight of the polymer to be relatively unchanged for samples prepared with or without MIPB, and we have already shown that the molecular weight is not affected by the presence of familiar

scintillating solutes (3). When samples of plastic scintillator similar in composition to those employed in pulse shape discrimination measurements were dissolved, and their molecular weights measured, it was found that a great reduction in molecular weight had occurred in comparison with polymers prepared in the absence of MIPB. These results indicated that MIPB was participating in the polymerization process, probably as a chain transfer agent. A formal investigation of the role of MIPB as a chain transfer agent was therefore initiated with the aim of determining: (a) the kinetic constants for chain transfer (b) their temperature dependence and hence activation energy (c) the relationship between the intrinsic viscosity and the number average molecular weight of polyvinyltoluene.

Before proceeding with the preliminary report of this investigation, it is probably advisable to review the basic steps in a vinyl polymerization reaction. The general features of these polymerizations are well established and are known to occur via a free radical mechanism involving the steps, initiation, propagation and termination. Once a free radical is formed by an initiator or by thermal means the whole process proceeds to completion with extreme rapidity, and the individual polymer radical has merely a fleeting existence. Consequently the reaction mixture at any instant consists of monomer and dead polymer together with an exceedingly small population of growing radicals. The dead, or full grown, polymer does not participate further in the reaction mechanism.

The reactions are succinctly summarized in Table I.

Table I

REACTION SCHEME FOR A VINYL POLYMERIZATION

	Rate Constant	Step	
$I \rightarrow 2R$	$k_d$	Initiation	1
$R. + M \rightarrow M_1.$	$k_p$	Propagation	2
$M_1. + M \rightarrow M_2$	$k_p$		
$M_x. + M \rightarrow M_{x+1}$	$k_p$		3
$M_x. + SH \rightarrow M_xH + S$	$k_{tr}$	Chain Transfer	4
$S. + M \rightarrow SM.$			
$M_x. + M_y. \rightarrow M_{x+y}$	$k_t$	Termination	5
or $M_x + M_y$			

The kinetics of chain transfer to solvents have been thoroughly investigated and it can be shown that

$$\frac{1}{x_n} = C_m + C_s [S] [M] + \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_I \frac{k_t}{k_p^2 k_d} \frac{R_p^2}{[M]^3} \quad \underline{6}$$

where  $C_m$ ,  $C_s$ ,  $C_I$  are chain transfer constants to monomer solvent and initiator respectively,

$k_t$ ,  $k_p$ ,  $k_d$  are rate constants for termination, propagation and initiation.

$[S]$ ,  $[M]$  are molar concentrations of solvent and monomer.  $R_p$  is the rate of the propagation reaction and  $x_n$  is the number average of monomer segments in the polymer.

If the third term is held constant, and chain transfer to monomer and initiator is negligible, (as is the case with styrene) then

$$\frac{1}{x_n} = \left( \frac{1}{x_n} \right)_0 + C_s \frac{[S]}{[M]} \quad \underline{7}$$

The latter equation is readily susceptible to experimental test. By plotting the reciprocal of the number average molecular weight against the solvent monomer ratio, S/M one can obtain  $C_s$ , the chain transfer constant from the slope of the linear relationship.

The term  $\frac{k_t}{k_p^2} \frac{R_p}{[M]^2}$  in equation 6 can be maintained constant

by adjusting the initiator concentration, by diluting with inert solvent which does not show chain transfer in a manner which does not alter the initiator or monomer concentrations, or by conducting a thermal polymerization with diradical initiation, as in styrene (4)(5).

## EXPERIMENTAL

Vinyltoluene monomer (Dow) was freed of inhibitor and distilled under reduced pressure. MIPB was acid washed, chromatographically purified, and distilled. For the thermally initiated samples, vials containing a total of 20 ml. of various ratios of monomer and MIPB were subjected to a series of freezing thawing cycles and sealed under vacuum. The samples were placed in thermostatted baths and allowed to polymerize to approximately 10% conversion at the chosen temperature.

Initiated samples were prepared as above, but contained a fixed concentration, 0.0609M of 2, 2'azobisisobutyronitrile, 10 ml of vinyl toluene and varying ratios of benzene and MIPB to furnish a total volume of 25 ml.

Molecular weights were determined by measurement of intrinsic viscosity and by direct determination employing a series of five Zimm-Myerson osmometers. Methyl ethyl ketone was used as solvent in each case.

## RESULTS

The results of thermal measurements are summarized in Table II for experiments performed at three temperatures. For the samples prepared at 60 and 100°C the polymerization was stopped at approximately 10% conversion and the samples were isolated by two precipitations from methyl ethyl ketone using methanol as precipitant. The 125°C samples were obtained from samples prepared previously in conjunction with pulse shape discrimination work and were completely polymerized. The results of the 125°C samples cannot strictly be compared with the other samples, because of complicating side effects at high conversion which partially invalidate the simple vinyl polymerization kinetic scheme here employed.

The chain transfer data are presented graphically in Figure 1, and it is seen that the results demonstrate the occurrence of chain transfer and allow a determination of the chain transfer constants. From these data and the temperature dependence of the chain transfer constants, it is in principle possible to predict the molecular weight of the polymer formed at any ratio of vinyl toluene to MIPB and at any temperature. The magnitude of the chain transfer effect

Table II

EVALUATION OF CHAIN TRANSFER CONSTANTS FOR THERMALLY INITIATED POLYMERS

Code	S		M	S/M	Viscosity		10 <sup>5</sup> /Xn	% Conversion	Intrinsic Viscosity
	Moles/l	Moles/l			Molecular Weight	%			
(60°C Thermal Sample)									
#1	0	9.506	0	0	1,371,000	8.63	11.6	1.414	
#2	.520	8.555	.0608	.0608	1,358,000	8.75	11.2	1.408	
#3	1.041	7.605	.1368	.1368	1,014,000	11.58	11.4	1.188	
#4	1.561	6.654	.2346	.2346	904,000	13.00	10.8	1.110	
#5	2.081	5.704	.3649	.3649	832,000	14.18	11.5	1.059	
#6	2.602	4.753	.5474	.5474	617,000	19.15	11.5	.890	
#7	3.122	3.802	.8210	.8210	513,000	23.05	10.2	.800	
#8	4.162	1.901	2.184	2.184	169,000	69.97	9.9	.420	
#9	4.683	0.9506	4.926	4.926	66,700	177.3	7.1	.245	
(100°C Thermal Samples)									
$C_s = 1.76 \times 10^4$									
#31	0	9.506	0	0	594,000	20.09	9.8	.871	
#32	0.520	8.555	.0608	.0608	513,000	22.46	10.4	.800	
#33	1.041	7.605	.1368	.1368	456,000	26.00	9.4	.748	
#34	1.561	6.654	.2346	.2346	405,000	29.55	9.2	.698	
#35	2.081	5.704	.3649	.3649	363,000	33.10	6.2	.656	
#36	2.602	4.753	.5474	.5474	295,000	40.19	7.0	0.580	
#37	3.122	3.802	.8210	.8210	220,000	53.19	8.5	.501	
$C_s = 3.9 \times 10^4$									

Table II  
(continued)

EVALUATION OF CHAIN TRANSFER CONSTANTS FOR THERMALLY INITIATED POLYMERS

Code	S		M		S/M	Viscosity Molecular Weight	$10^5/X_n$	% Conversion	Intrinsic Viscosity
	Moles/l		Moles/l						
IP-10	0		9.506		0	515,000	22.46	100	.801
IP-11	0.520		8.555		.0608	258,000	44.92	100	.554
IP-12	1.041		7.605		.1368	224,000	53.19	100	.494
IP-14	2.081		5.704		.3649	117,000	101.65	100	.342
IP-15	2.602		4.753		.5474	85,700	137.11	100	.283

(125°C Thermal Samples)

$$C_s = 21.5 \times 10^4$$

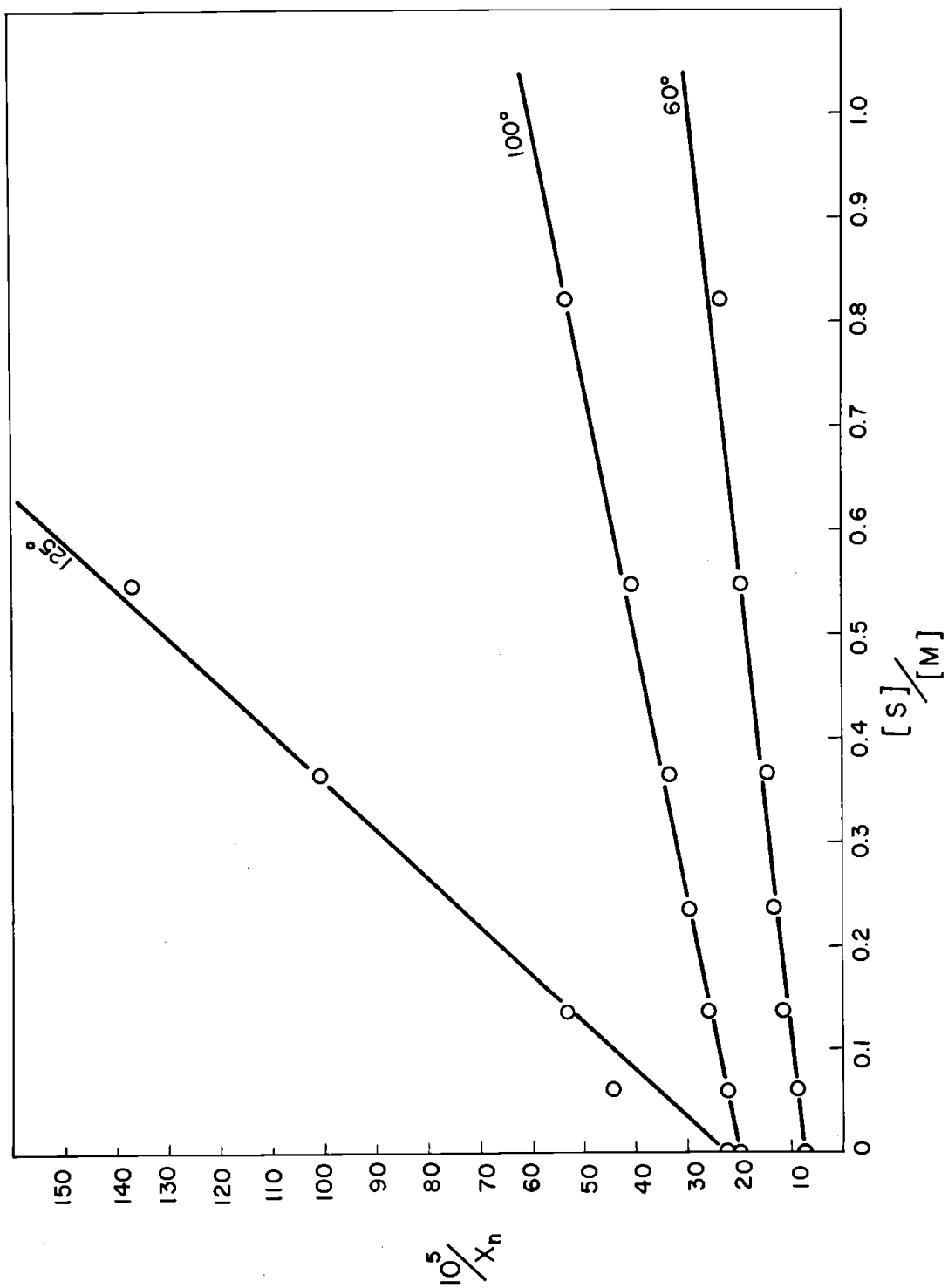


Fig. 1. Chain transfer with MIPB.

is surprisingly large, and indeed it can be seen that a sixfold reduction in molecular weight was obtained for sample IP-15 in Table II at a relatively low S/M ratio of .55 . The chain transfer constant at 60° is exactly 100 times that of benzene with styrene at this temperature.

We expect to complete the measurement of the initiated samples in the near future, and thus obtain an independent check of the chain transfer constants and also a better value for the energy of activation. However, the general pattern of these systems is already clear and we are confident that chain transfer plays a major role in the polymerization of samples containing MIPB.

Detailed investigations of plastic scintillators have often been hampered by the lack of any reported value relating the intrinsic viscosity of polyvinyltoluene to the molecular weight of this polymer. If the constants K and  $\alpha$  in the Staudinger equation

$$N = KM^{\alpha} \quad \underline{g}$$

are known then for many investigations simple viscosity measurements for a series of concentrations serve to determine molecular weight.

As part of this work we undertook the evaluation of these parameters employing the osmometers which we are using in our laboratory (7). Only preliminary values can be presented at this time, since the measurements required lengthy equilibration times and the work was initiated quite recently. However the relationship

$$N = 2.86 \times 10^{-6} M_n^{.99}$$

appears to be a satisfactory one for relating number average molecular weight to intrinsic viscosity of polyvinyl toluene. The logarithmic plot of log M vs log N from which this was obtained by the method of least squares is shown in Figure 2.

#### QUENCHING STUDIES IN LIQUID SCINTILLATORS

A systematic study has been made of the kinetics of the quenching process in liquid scintillators containing MIPB or toluene as solvents. The kinetic scheme and rate constants shown in Table III were postulated and by the application of a steady state treatment the following relationships were obtained.

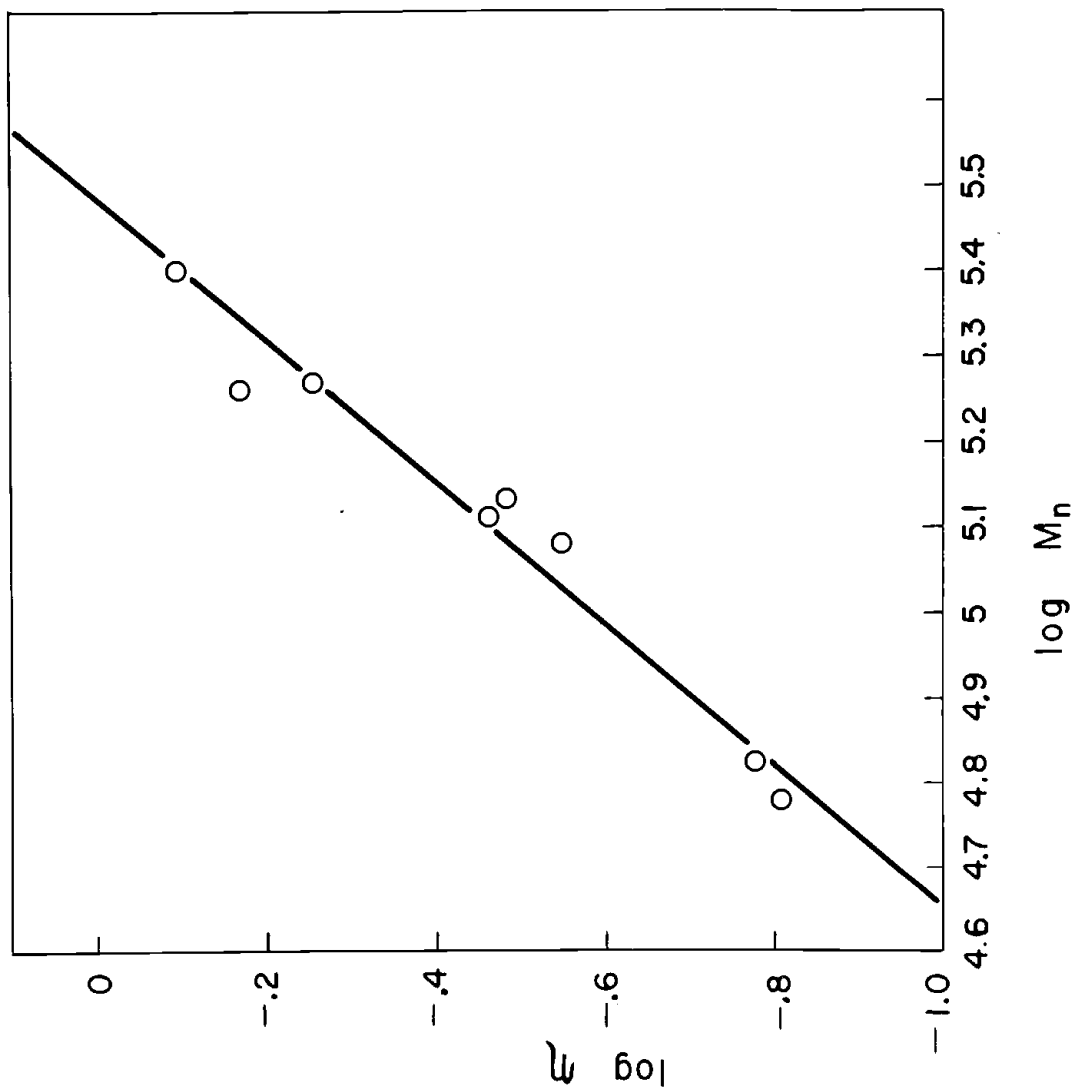


Fig. 2. Dependence of number of average molecular weight on intrinsic viscosity.

Table III

KINETIC SCHEME FOR ENERGY TRANSFER

$S + h\nu$	$S^*$		Excitation
$S^* + S$	$2S$	$k_s$	Solvent quenching
$S^* + S$	$S^* + S$	$k_t$	Propagation
$S^* + F$	$F^* + S$	$k_p$	Transfer to solute
$F^*$	$F + h\nu$	$k_r$	Solute emission
$F^* + F$	$2F$	$k_i$	Internal quenching
$F^* + Q$	$FQ$	$k_q$	External quenching of solute
$S^* + Q$	$S + Q$	$k_m$	External quenching of solvent
$S^*$	$S + h\nu$		Solvent emission

$$V = \frac{k_r k_p I [F]}{k_r + k_i [F] + k_p [F] + k_s [S] + k_m [Q]} \quad \underline{10}$$

and

$$\frac{V}{V_0} - 1 = \frac{k_m [Q]}{k_p [F] + k_s S} \quad \underline{11}$$

where S, F and Q refer to the molar concentrations of solvent, phosphor and quencher and I is the incident flux of ionizing radiation and V, V<sub>0</sub> are the intensities of emitted light, in the presence or absence of Q.

Equation 11 is formally similar to the Stern Volmer equation (8) employed in fluorescence studies and the quenching constant

$$y'' = \frac{k_m}{k_p [F] + k_s [S]} \quad \underline{12}$$

It is evident that a plot of 1/y'' vs F should be linear and its slope will determine k<sub>p</sub>/k<sub>m</sub> and intercept k<sub>s</sub> S/k<sub>m</sub>. The slope to intercept ratio serves to evaluate k<sub>p</sub>/k<sub>s</sub>S and this ratio should thus be independent of the quenching agent employed but should be influenced by the nature of the solvent. This ratio is similar to the ratio E/A employed by Hardwick (9). The experimental work was undertaken in order to test this point and to obtain quenching constants and other rate constants in these liquid scintillator systems.

#### EXPERIMENTAL

Procedures and apparatus were identical to those reported in previous papers (3)(2). The choice of quenching agents reflected our interest in loading liquid scintillators with elements of high atomic number. Diphenyl mercury (DPHg), and lead 2-ethyl-hexanoate were therefore chosen for this study as well as CCl<sub>4</sub>. The latter was employed for comparison with existing data on the high quenching action of halogenated compounds.

## RESULTS

From the work with two solvents, three quenching agents and two solutes, twelve sets of quenching curves were obtained. Two representative sets of data are shown in Figure 3 and 4 where the data for the quencher diphenyl mercury are plotted as a function of quencher concentration at the inscribed concentrations of terphenyl as primary solute. The concentrations on POPOP was maintained at 0.05 g/l.

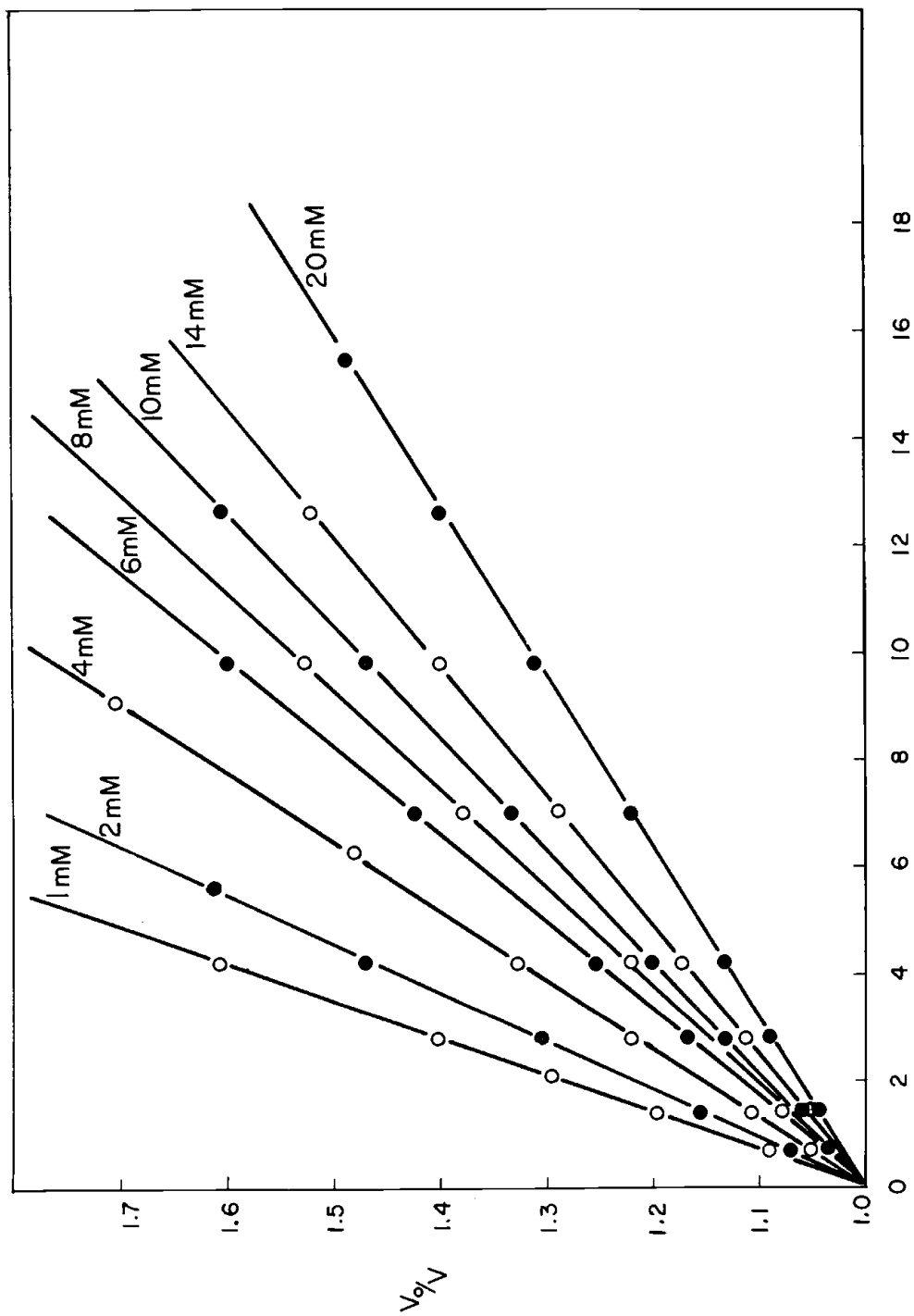
It is immediately obvious from the slopes of the various lines that the quenching constants are significantly lower in MIPB than in toluene and the various quenching constants are assembled in Table IV. These quenching constants have been plotted against phosphor concentration in order to test the validity of equation 12. A typical plot is shown in Figure 5 and the data for all the systems investigated are summarized in Table V. The ratio of intercept to slope is found to be independent of the quencher employed and is interpreted as being the ratio of  $k_s/k_m$ . This ratio differs significantly for MIPB and toluene and in view of the difficulties of comparison of quantities based on a slope of a slope the agreement in results appears quite satisfactory. The data are consistent with results obtained by other workers (9) (10).

In conclusion we can state that MIPB behaves as an efficient chain transfer agent in plastic scintillators and one can conjecture that the pulse shape discrimination properties shown by these are related to the lower molecular weights which they possess and its different distribution. The chain length constants obtained and their temperature dependence make possible a prediction of the number average molecular weight for any composition of polymer over a wide range of polymerization temperatures.

For liquid scintillators based on MIPB as solvent, quenching constants have been determined and compared with the higher values obtained for toluene. A kinetic scheme has been postulated which has been substantially verified by the experimental results obtained by variation of the concentration of solute and quencher.

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Concentration [Cq] (mMoles/l) of Diphenyl Hg in toluene -terphenyl - POPOP

Fig. 3. Quenching by diphenyl mercury at the inscribed concentration of terphenyl in toluene.

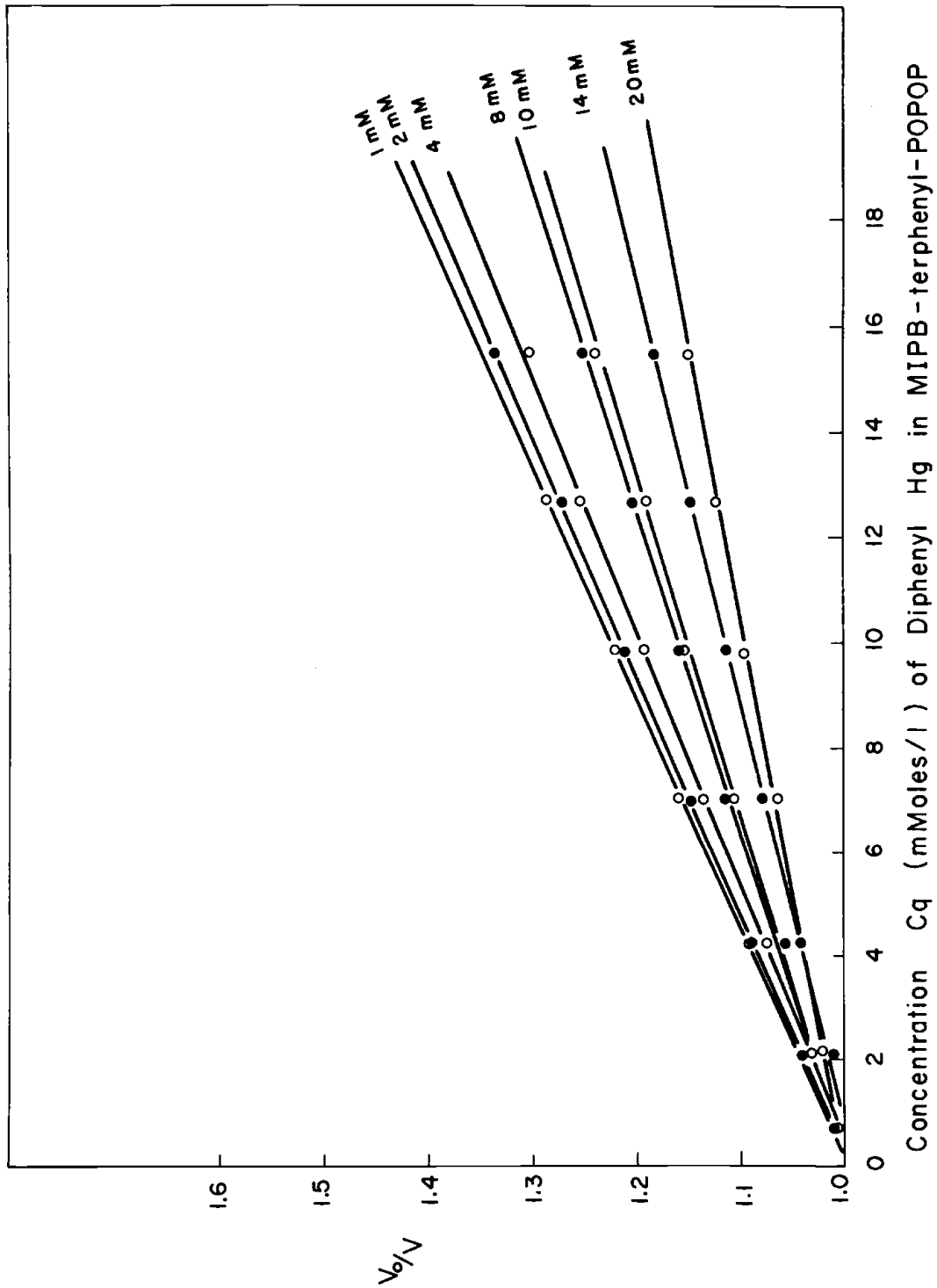


Fig. 4. Quenching by diphenyl mercury at the inscribed concentration of terphenyl in MIPB.

Table IV

QUENCHING CONSTANTS

System	Solvent	Toluene				MIPB			
		Conc'n F (Moles/l)	V (%)	Vo/V (l/Mole)	Y'' (l/Mole)	V (%)	Vo/V (l/Mole)	Y'' (l/Mole)	
Terphenyl- CCl <sub>4</sub> (.005 Moles/l)		.001	10.9	1.818	163.6	21.9	1.378	75.6	
		.002	17.1	1.695	139.0	25.7	1.359	71.8	
		.004	23.8	1.547	119.4	30.0	1.335	67.0	
		.006	27.9	1.462	92.4	33.0	1.290	58.0	
		.008	31.4	1.415	83.0	35.2	1.263	52.6	
		.010	33.4	1.381	76.2	37.6	1.242	48.4	
		.014	35.4	1.353	70.6	40.1	1.191	38.2	
		.020	39.3	1.286	57.2	41.7	1.186	37.2	
	PBD - CCl <sub>4</sub> (.005 Moles/l)		.001	11.8	1.807	161.4	23.4	1.524	104.8
			.002	17.4	1.647	129.4	27.3	1.412	82.4
		.004	25.9	1.493	98.6	33.9	1.315	63.0	
		.006	31.6	1.383	76.6	36.9	1.277	55.4	
		.008	35.0	1.312	62.4	38.7	1.240	48.0	
		.010	35.9	1.286	57.2	39.9	1.205	41.0	
	.014	39.5	1.254	50.8	43.4	1.168	33.6		
	.020	43.6	1.175	35.0	43.6	1.150	30.0		

Table IV - Page 2

QUENCHING CONSTANTS

System	Solvent	Toluene				MIPB			
		Conc'n F (Moles/l)	V (%)	Vo/V	Y'' (l/Mole)	V (%)	Vo/V	Y'' (l/Mole)	
Terphenyl Pb-2-Et- Hex. (.005 Moles/l)		.001	15.2	1.295	59.1	26.6	1.130	26.0	
		.002	22.9	1.265	52.9	30.6	1.127	25.0	
		.004	30.6	1.197	40.4	35.7	1.110	22.0	
		.006	35.2	1.151	30.4	38.7	1.098	20.0	
		.008	39.3	1.130	26.1	40.6	1.092	18.4	
		.010	42.0	1.107	21.7	43.0	1.084	16.9	
		.014	44.4	1.085	17.0	44.8	1.072	14.8	
		.020	47.0	1.078	16.0	47.7	1.048	12.0	
PBD Pb-2-Et- Hex. (.005 Moles/l)		.001	17.1	1.254	49.9	31.8	1.112	22.4	
		.002	23.8	1.233	46.4	34.8	1.105	20.5	
		.004	32.6	1.181	35.7	41.0	1.087	17.2	
		.006	38.0	1.143	28.3	43.4	1.083	16.6	
		.008	41.1	1.120	24.4	44.7	1.075	14.5	
		.010	41.8	1.113	22.5	45.5	1.067	13.3	
		.014	46.2	1.080	15.1	47.2	1.054	10.9	
		.020	47.8	1.068	12.5	48.0	1.043	9.0	

Table IV - Page 3

QUENCHING CONSTANTS

System	Solvent	Toluene				MIPB			
		Conc'n F (Moles/l)	V (%)	Vo/V	Y'' (l/Mole)	V (%)	Vo/V	Y'' (l/Mole)	Y'' (l/Mole)
Terphenyl DPHg. - (.005 Moles/l)		.001	11.5	1.715	143.0	27.0	1.112	22.4	
		.002	18.7	1.547	109.4	31.6	1.107	21.4	
		.004	26.5	1.387	77.4	36.3	1.097	19.4	
		.006	31.2	1.304	6	39.2	1.085	17.0	
		.008	35.0	1.269	53.8	41.3	1.080	16.0	
		.010	37.4	1.237	47.4	43.5	1.075	15.0	
		.014	39.8	1.206	41.2	45.0	1.061	12.2	
		.020	43.7	1.157	31.4	47.4	1.049	9.8	
PBD - DPHg. - (.005 Moles/l)		.001	14.1	1.510	102.0	31.6	1.126	25.2	
		.002	20.1	1.425	85.0	35.2	1.097	19.4	
		.004	29.2	1.322	64.4	41.4	1.077	15.4	
		.006	35.0	1.252	50.4	44.2	1.067	13.4	
		.008	37.7	1.222	44.4	45.3	1.060	12.0	
		.010	39.1	1.180	36.0	45.7	1.055	11.0	
		.014	43.4	1.146	29.2	47.6	1.046	9.2	
		.020	45.5	1.127	25.4	48.8	1.037	7.4	

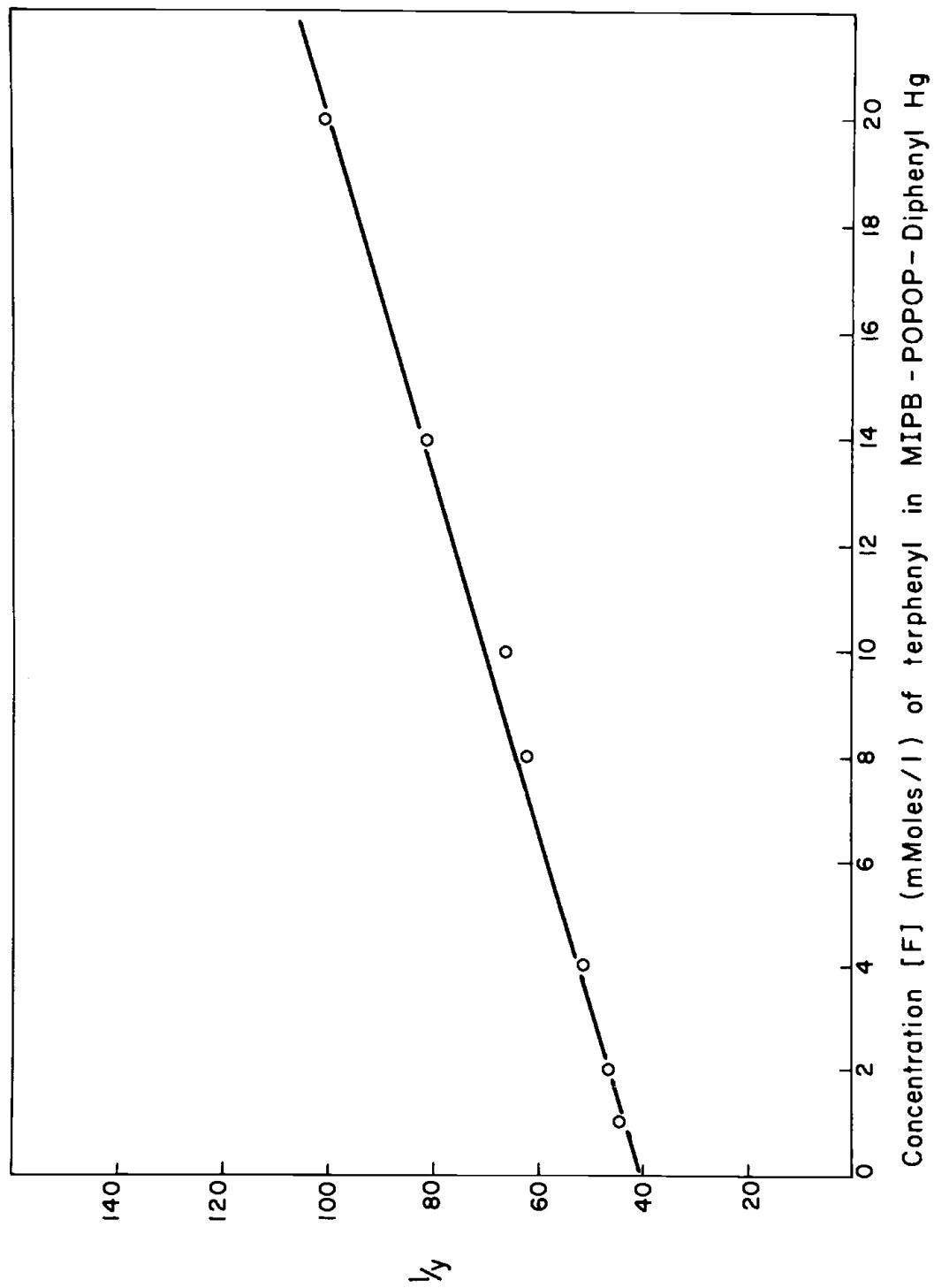


Fig. 5. Dependence of quenching constants on phosphor concentration.

Table V

EVALUATION OF PARAMETERS FROM QUENCHING DATA

Solute- Quenching System	TOLUENE		MIPB	
	Intercept kSS/km (moles/l)	Slope kp/km	Intercept/slope kSS/kp = Q (moles/l)	Intercept/slope Slope kSS/kp=Q kp/km (moles/l)
PBD - CCl <sub>4</sub>	$5.0 \times 10^{-3}$	1.24	$4.0 \times 10^{-3}$	$9.5 \times 10^{-3}$ 1.44 $6.3 \times 10^{-3}$
PBD - Pb-2- Et-Hex	$15.0 \times 10^{-3}$	3.48	$4.3 \times 10^{-3}$	$42.2 \times 10^{-3}$ 3.36 $12.6 \times 10^{-3}$
PBD - DPHg	$8.0 \times 10^{-3}$	1.95	$4.3 \times 10^{-3}$	$49.0 \times 10^{-3}$ 4.18 $11.7 \times 10^{-3}$
Terphenyl - CCl <sub>4</sub>	$5.1 \times 10^{-3}$	0.97	$5.3 \times 10^{-3}$	$12.2 \times 10^{-3}$ 0.84 $14.5 \times 10^{-3}$
Terphenyl - Pb- 2-ET-Hex	$13.5 \times 10^{-3}$	3.17	$4.3 \times 10^{-3}$	$35.2 \times 10^{-3}$ 2.47 $14.3 \times 10^{-3}$
Terphenyl - DPHg	$6.5 \times 10^{-3}$	1.51	$4.3 \times 10^{-3}$	$40.7 \times 10^{-3}$ 2.98 $13.7 \times 10^{-3}$

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