

Determination of Propagation and Termination Rate Constants for Some Methacrylates in Their Radical Polymerizations

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Synopsis

Rotating sector determinations of k_p and $2k_t$ for ten methacrylates undergoing radical polymerization were carried out at 30°C. Ester groups in the monomers were: isopropyl, ethyl, β -cyclohexylethyl, methyl, γ -phenylpropyl, β -phenylethyl, β -methoxyethyl, benzyl, β -chloroethyl, and phenyl. Values of k_p obtained were 121, 126, 1190, 141, 149, 228, 249, 1250, 254, and 411 l./mole-sec., respectively; values of $2k_t \times 10^{-6}$ were 4.52, 7.35, 32.8, 11.6, 0.813, 1.88, 9.30, 41.9, 6.71, and 11.9 l./mole-sec., respectively.

Omitting the data for the β -cyclohexylethyl and benzyl esters, a Taft correlation, $\log k_p = (0.70 \pm 0.18)\sigma^* + 2.2$, was established, where σ^* denotes Taft's polar substituent constants for the above-mentioned ester groups. The steric substituent constants E_s were found to have no influence on k_p . Combination of k_p with r_2 data from copolymerization studies with styrene or methyl methacrylate as M_1 comonomer revealed that the more reactive monomer gave rise to the more reactive polymer radical. Monomer viscosities and molar volumes of the ester groups were found to correlate with $2k_t$.

INTRODUCTION

A satisfactory, precise quantitative correlation of reactivities of vinyl monomers and of derived radicals with their structures has not yet been achieved. In the homopolymerization process, the rate of propagation of a given monomer involves two separate reactivities, i.e., that of monomer and that of the derived radical; the latter is considered to be more important. Hence as a whole, a monomer with larger resonance contribution is more reactive, gives rise to a less reactive radical, and consequently shows a smaller k_p value.

A detailed correlation requires a study of monomers in which systematic structural variations have been made. Recent studies by Imoto et al.^{1,2} on *p*-substituted styrenes established the Hammett correlations of propagation rate constants, of reactivities of monomers, and of derived radicals. In this paper, a rotating sector determination of a series of methacrylate monomers is described, and Taft correlations of k_p and of derived radical reactivities are discussed. Termination rate constants $2k_t$ were also correlated with monomer structures.

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EXPERIMENTAL

Preparation and Purification of Monomers

Methyl methacrylate was kindly supplied by the Mitsubishi Rayon Co. Ltd. Ethyl methacrylate was the commercially available product. β -Cyclohexylethyl, γ -phenylpropyl, β -phenylethyl, β -methoxyethyl, benzyl, and β -chloroethyl methacrylates were prepared in nearly quantitative yields by ester exchange between appropriate alcohols and a 4*M* excess of methyl methacrylate free from inhibitor in the presence of a small amount of *p*-toluenesulfonic acid as a catalyst. Isopropyl methacrylate was prepared similarly but with an excess of isopropyl alcohol. Phenyl methacrylate was prepared by the reaction of methacryl chloride and sodium phenoxide in water. The crude monomers were repeatedly fractionated through a Widmer column under nitrogen at reduced pressure until impurities (mostly alcohols) were not detected by gas chromatography. Non-volatile cuprous chloride was used as inhibitor. Monomers were identified by their boiling points, refractive indices, infrared, ultraviolet, and nuclear magnetic resonance spectra, as well as elementary analyses for some polymers. These results are given in part in Table I.

The monomers thus prepared were washed with saturated sodium bisulfite, 5% sodium hydroxide, 20% sodium chloride, and distilled water successively, dried over anhydrous sodium sulfate, distilled, and stored in a refrigerator. They were again distilled after prepolymerization immediately before use.

Other Reagents

α,α' -Azobisisobutyronitrile (AIBN), commercially available, was recrystallized twice from ethyl alcohol, m.p. 102–103°C. α,α' -Azobiscyclohexanecarbonitrile was prepared according to Overberger's description⁴ and recrystallized twice from ethyl alcohol, m.p. 113–114°C. β,β -Diphenyl- α -picrylhydrazyl (DPPH), commercially available, was recrystallized twice from benzene–petroleum ether and obtained as the benzene complex, m.p. 132–133°C. Benzene was successively washed with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water, dried over calcium chloride, and fractionated under nitrogen.

Density Measurements

Densities of monomers and monomer–polymer mixtures were measured in a pycnometer at 30.0°C., and the results were used to calibrate the dilatometry.

Viscosity Measurements

Viscosities of monomers were measured at 30.0°C. with an Ostwald viscometer. Solution viscosities of polymers (η_{sp}/c) were measured also with an Ostwald viscometer at the same temperature in benzene, $c = 0.3$ g./100 ml.

TABLE I
Properties of Monomers^a

Ester group	Boiling point, °C./mm. Hg	n_D^{25}	d_{40}^{30} , g./cc.	d_{40}^{30} , g./cc.	η_{monomer} , cP.	Found ^b C, %	H, %	Calcd. C, %	H, %
Isopropyl	65-67/95 (120/760)	1.4107 ²⁰ (1.4122 ²⁰)	0.8765	1.0505	0.610	65.35	9.16	65.59	9.44
Ethyl	116-117/760 (116-117/760)	1.4120 ²¹ (1.4147 ²⁰)	0.9045 (0.9135 ²⁰)	1.0795	0.565				
β -Cyclohexylethyl	99-102/3	1.4641 ¹⁸	0.9423	1.0613	2.79	73.81	10.30	73.43	10.27
Methyl	33-34/55 (100/760)	1.4163 ²¹ (1.4162 ²⁰)	0.9296 (0.9313)	1.2036 (1.1834)	0.516				
γ -Phenylpropyl	108-114/3	1.5034 ²¹	0.9967	1.1097	3.42				
β -Phenylethyl	100-105/3 (110-117/5)	1.5058 (1.0018)	1.0123 (1.0018)	1.1427	2.98				
β -Methoxyethyl	75-76/22 (65-67/10)	1.4280 ²¹ (1.4283 ²⁴)	0.9818 (0.990 ²⁰)	1.1378 1.18	1.03	57.65	8.33	57.31	8.39
Benzyl	88-90/3 (104-106/6)	1.5112 ²¹ (1.514 ²⁰)	1.0299	1.1819	2.09				
β -Chloroethyl	81-85/42 (61-64/11)	1.4498 ¹⁸ (1.4515 ²⁰)	1.0942 (1.106 ²⁰)	1.3002	0.933	49.02	6.21	48.50	6.11
Phenyl	81-82/5 (83-84/4)	1.5149 ²¹ (1.5156 ²⁰)	1.0485 (1.053 ²⁰)	1.1665	3.14	73.77	6.45	74.05	6.21

^a Values in parentheses are literature values.²

^b Analysis of polymer samples.

Rate of Polymerization

Rates of polymerization were followed by dilatometry. Gravimetric experiments in sealed ampules gave satisfactory agreement with dilatometric results.

Rate Dependences on Monomer Concentration and on Initiator Concentration

Those experiments were carried out at $30.0 \pm 0.005^\circ\text{C}$. in the dark in a 10-ml. glass ampule connected with a capillary tube. Freshly distilled monomer, AIBN, and benzene were taken in a calibrated ampule. The contents were subjected to repeated freezing, pumping, and thawing under nitrogen (purified on hot copper net) and finally *in vacuo*. Then the contents were transferred to a polymerization ampule *in vacuo*, sealed off, and subjected to polymerization in a bath at a constant temperature. The concentration of initiator was $2\text{--}20 \times 10^{-2}$ mole/l. in neat monomer. The concentration of monomer examined ranged from bulk to 1 mole/l. in benzene.

Rate of Initiation

Rates of initiation were determined under the same conditions as above but with a small amount of DPPH in 80 vol.-% of monomer in benzene and calculated from the inhibition periods and the amounts of added inhibitor.

Radical Lifetime

Radical lifetimes were determined by the rotating sector method. Polymerizations were carried out in thin drum-shaped Pyrex ampules by use of azobiscyclohexanecarbonitrile as sensitizer under illumination with a 300 w. mercury lamp through a slit and a Toshiba UVD1C filter (passes 340–380 $m\mu$). The sector was made of a 60-cm. diameter black aluminum disk cut off at two positions so that the dark to light period ratio was three. The sector was driven by a 10-w. reaction synchronous motor 4SQ10 (Oriental Motor Co. Ltd.) and its speeds were accurately varied by using several combinations of gear heads (supplied by the same maker). Corrections for the dark rates were made according to the equations derived by Matheson et al.⁵ [eqs. (6), (7), and (8) in their paper]. Computed figures for the corrections are collected in Table II.

Copolymerization

Copolymerizations with styrene or methyl methacrylate were carried out for isopropyl and β -methoxyethyl methacrylates at 60°C . with AIBN to less than 10% conversions. Copolymer compositions were calculated from carbon contents for styrene copolymers and from appropriate NMR peak area ratios for methyl methacrylate copolymers.

TABLE II
Theoretical Values of $(p + 1)^{1/2}R_{pi}/R_p$, $p = 3$ as a Function of Flash Time t and Dark Rate/Steady Light Rate $n^{1/2}$ ^a

Flash time t , sec.	$(p + 1)^{1/2}R_{pi}/R_p$																	
	$n^{1/2} = 0$	$n^{1/2} = 0.01$	$n^{1/2} = 0.02$	$n^{1/2} = 0.03$	$n^{1/2} = 0.04$	$n^{1/2} = 0.05$	$n^{1/2} = 0.06$	$n^{1/2} = 0.07$	$n^{1/2} = 0.08$	$n^{1/2} = 0.09$	$n^{1/2} = 0.10$	$n^{1/2} = 0.11$	$n^{1/2} = 0.12$	$n^{1/2} = 0.13$	$n^{1/2} = 0.14$	$n^{1/2} = 0.15$	$n^{1/2} = 0.16$	$n^{1/2} = 0.17$
0.1	0.9991	0.9992	0.9997	1.0004	1.0015	1.0028	1.0045	1.0064	1.0086	1.0112	1.0140	1.0171	1.0205	1.0242	1.0281	1.0323	1.0368	1.0415
0.2	0.9963	0.9965	0.9969	0.9977	0.9987	1.0001	1.0017	1.0036	1.0059	1.0085	1.0113	1.0145	1.0178	1.0216	1.0255	1.0298	1.0343	1.0389
0.3	0.9919	0.9920	0.9925	0.9932	0.9943	0.9957	0.9974	0.9993	1.0016	1.0042	1.0070	1.0102	1.0136	1.0174	1.0214	1.0257	1.0301	1.0345
0.5	0.9787	0.9789	0.9794	0.9802	0.9813	0.9827	0.9844	0.9865	0.9888	0.9915	0.9944	0.9977	1.0012	1.0051	1.0092	1.0137	1.0181	1.0224
0.7	0.9616	0.9618	0.9623	0.9631	0.9643	0.9658	0.9676	0.9697	0.9722	0.9749	0.9780	0.9814	0.9852	0.9892	0.9935	0.9981	1.0024	1.0066
1	0.9326	0.9328	0.9333	0.9342	0.9355	0.9371	0.9390	0.9414	0.9440	0.9470	0.9504	0.9541	0.9581	0.9625	0.9671	0.9721	0.9764	0.9806
2	0.8440	0.8442	0.8450	0.8462	0.8479	0.8501	0.8528	0.8559	0.8595	0.8636	0.8681	0.8730	0.8784	0.8841	0.8903	0.8968	0.9030	0.9091
3	0.7838	0.7842	0.7851	0.7867	0.7889	0.7918	0.7952	0.7993	0.8039	0.8090	0.8147	0.8209	0.8276	0.8347	0.8423	0.8503	0.8584	0.8664
5	0.7140	0.7145	0.7159	0.7182	0.7214	0.7255	0.7304	0.7361	0.7425	0.7496	0.7573	0.7656	0.7744	0.7836	0.7933	0.8034	0.8135	0.8235
7	0.6745	0.6751	0.6769	0.6800	0.6841	0.6894	0.6956	0.7027	0.7106	0.7191	0.7283	0.7381	0.7483	0.7590	0.7700	0.7814	0.7928	0.8041
10	0.6386	0.6395	0.6420	0.6460	0.6515	0.6583	0.6661	0.6748	0.6844	0.6945	0.7053	0.7164	0.7280	0.7399	0.7521	0.7645	0.7769	0.7891
20	0.5858	0.5874	0.5919	0.5989	0.6076	0.6176	0.6286	0.6402	0.6523	0.6648	0.6777	0.6907	0.7040	0.7175	0.7310	0.7448	0.7584	0.7719
30	0.5638	0.5661	0.5723	0.5813	0.5918	0.6034	0.6157	0.6285	0.6416	0.6549	0.6684	0.6822	0.6960	0.7100	0.7240	0.7382	0.7519	0.7654
50	0.5433	0.5469	0.5556	0.5668	0.5791	0.5921	0.6054	0.6191	0.6329	0.6469	0.6611	0.6753	0.6896	0.7040	0.7184	0.7329	0.7469	0.7606
70	0.5333	0.5380	0.5483	0.5606	0.5737	0.5872	0.6010	0.6151	0.6292	0.6435	0.6579	0.6724	0.6869	0.7014	0.7160	0.7306	0.7444	0.7579
100	0.5251	0.5312	0.5428	0.5559	0.5696	0.5835	0.5977	0.6120	0.6265	0.6410	0.6555	0.6701	0.6848	0.6995	0.7142	0.7290	0.7434	0.7574
200	0.5143	0.5231	0.5364	0.5504	0.5648	0.5793	0.5939	0.6085	0.6232	0.6380	0.6528	0.6676	0.6824	0.6972	0.7121	0.7270	0.7414	0.7554
300	0.5102	0.5204	0.5343	0.5486	0.5632	0.5778	0.5926	0.6073	0.6222	0.6370	0.6518	0.6667	0.6816	0.6965	0.7114	0.7263	0.7407	0.7550

^a According to eqs. (6), (7), and (8) of Matheson et al.⁵ R_p = rate of polymerization in steady light, R_{pi} = rate of polymerization in flash time t ; p = dark to light period ratio.

RESULTS

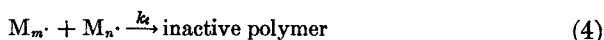
From the rate dependences on initiator and monomer concentrations collected in Table III, it is clear that the present polymerizations can be treated by the four simple reactions given in eqs. (1)–(4).



with $R_i = 2k_d f [I]$



with $R_p = k_p [M_j \cdot] [M] = k_p (k_d f / k_t)^{1/2} [M] [I]^{1/2}$



with $R_t = 2k_t [M \cdot]^2$

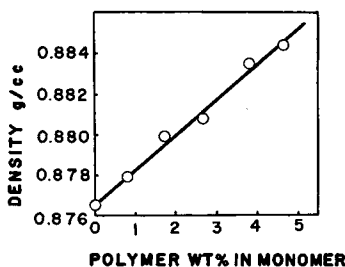


Fig. 1. Densities of monomer and monomer-polymer mixtures for isopropyl methacrylate.

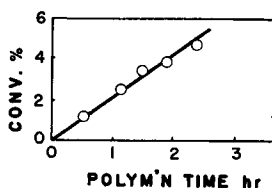


Fig. 2. Comparison of (—) dilatometric and (O) gravimetric determinations of rate of polymerization for isopropyl methacrylate.

Because of the kinetic results and of the fairly high specific viscosities of isolated polymers (Table III), degradative chain transfer or other unimolecular terminations are not important. Rate dependences on monomer concentration were over unity for some monomers, and in such cases, however, it had been consistently attributed to the complication in the initiation stage⁶ and also need not be considered here. Since rates of polymerization after the consumption of DPPH were only slightly smaller than that without inhibitor, the rate of initiation R_i and the radical lifetime τ determined separately were combined to calculate the propagation rate

TABLE III
Rate Constants and Related Quantities for the Radical Polymerizations of Methacrylates at 30°C.

Ester group	m^a	n^a	$R_i \times 10^3$, mole/l.-sec. ^b	f^c	$k_p^2/2k_t \times 10^3$, l./mole-sec.	τ , sec. ^d	$k_p/2k_t \times 10^5$	k_p , l./mole-sec.	$2k_t \times 10^{-6}$, l./mole-sec.	η_{sp}/c , dl./g. ^e
Isopropyl	1.00	0.50	9.30	0.69	3.22	2.30	2.67	121	4.52	4.3
Ethyl	1.00	0.50	10.1	0.74	2.17	1.84	1.72	126	7.35	3.6
β -Cyclohexylethyl	1.12	0.50 _s	2.85	0.22	43.0	1.29	3.63	1190	32.8	6.1
Methyl	1.00	0.50	8.25	0.63	1.71	1.56	1.21 _s	141	11.6	3.9
γ -Phenylpropyl	1.00	0.51	5.00	0.38	27.0	5.90	18.1	149	0.813	6.4
β -Phenylethyl	1.11	0.50	6.78	0.52	27.6	4.81	12.3	228	1.88	3.2
β -Methoxyethyl	0.98	0.52	8.33	0.63	6.67	1.40	2.68	249	9.30	1.2
Benzyl	1.15	0.51	3.62	0.27	37.5	1.26	2.99	1250	41.9	5.4
β -Chloroethyl	1.00	0.50	7.63	0.58	9.95	2.70	3.85	254	6.71	1.2
Phenyl	1.10	0.50	7.93	0.60	15.3	1.70	3.46	411	11.9	3.2

^a In $R_p = k_p(k_{af}/k_t)^{1/2}[M]^{1/2}[I]^{1/2}$.

^b $[I] = 5 \times 10^{-7}$ /sec. $[M] = 80$ vol.-% in benzene.

^c $k = 1.31 \times 10^{-7}$ /sec. assumed, $f = R_i/2k_d[I]$.

^d $[I] = 4.10 \times 10^{-3}$ mole/l., monomer bulk.

^e Measured in benzene at 30°C., $c = 0.3$ g./100 ml. for the polymer obtained at $[I] = 5 \times 10^{-3}$ mole/l., $[M] = 80$ vol.-% in benzene.

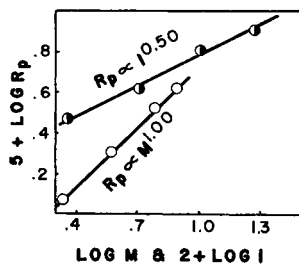


Fig. 3. Rate dependences on (●) initiator concentration and (○) on monomer concentration for isopropyl methacrylate.

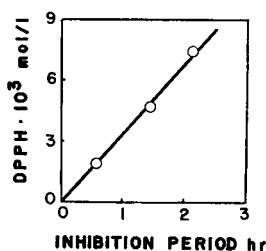


Fig. 4. Determination of rate of initiation for isopropyl methacrylate.

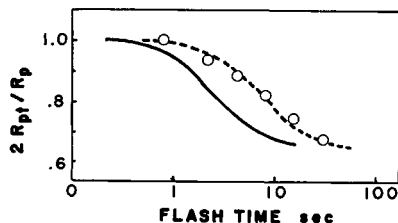


Fig. 5. Determination of radical lifetime for isopropyl methacrylate: (—) $\tau = 1$ sec., dark rate/steady light rate = 0.07; (---) $\tau = 2.30$ sec. (R_p = rate of polymerization in steady light, $R_{p,t}$ = rate of polymerization in flash time t .)

constant k_p and the termination rate constant $2k_t$ according to eqs. (5) and (6):

$$k_p^2/2k_t = R_p^2/R_i[M]^2 \quad (5)$$

$$k_p/2k_t = R_p\tau/[M] \quad (6)$$

Typical results of a series of experiments are shown in Figures 1–5 for isopropyl methacrylate, and satisfactory plots are observed. All results are summarized in Table III.

For methyl methacrylate, $k_p = 141$ l./mole-sec. and $2k_t = 11.6 \times 10^6$ l./mole-sec. are obtained. These values are in good accordance with the values, $k_p = 143$ l./mole-sec. and $2k_t = 12.2 \times 10^6$ l./mole-sec. at 30°C. reported by Matheson et al.,⁵ whose description of the apparatus and

calculation we followed. We estimate, however, that the accumulated experimental errors may amount to about $\pm 40\%$ at the final k_p and $2k_t$ values.

The more important problem is the discrepancies among reported k_p values far beyond the experimental errors for a given monomer by several investigators. For example, Table IV shows the compiled k_p values⁷ for

TABLE IV
 k_p for Methyl Methacrylate^a

k_p , l./mole-sec.	Temperature, °C.	Method
143	30	Rotating sector
310 \pm 20	23.6	"
410 \pm 50	35.9	"
248	30	"
512.6	25	"
128	22	Single period, highly sensitive dilatometer
106	32	Single period, thermocouple
384	22.5	" "

^a Literature values for k_p .⁷

methyl methacrylate at about 30°C. There is a fivefold difference between the largest and the smallest values. Matheson⁸ thoroughly discussed this problem, without fully revealing the cause. We consider that a series of experiments by one investigator's apparatus would greatly minimize systematic errors at least, and the results of such experiments should be useful for the discussion of the relative reactivities.

Copolymerization experiments afforded the following four sets of monomer reactivity ratios obtained by the Fineman-Ross plots. Errors were calculated at the level of 95% confidence: For styrene (M_1) and isopropyl methacrylate, $r_1 = 0.47 \pm 0.06$ and $r_2 = 0.74 \pm 0.05$; for styrene (M_1) and β -methoxyethyl methacrylate, $r_1 = 0.50 \pm 0.01$ and $r_2 = 0.58 \pm 0.04$; for methyl methacrylate (M_1) and isopropyl methacrylate, $r_1 = 0.89 \pm 0.21$ and $r_2 = 1.20 \pm 0.20$; for methyl methacrylate (M_1) and β -methoxyethyl methacrylate, $r_1 = 0.86 \pm 0.11$ and $r_2 = 1.06 \pm 0.11$.

DISCUSSION

From the individual rate constants of ten methacrylates as summarized in Table III, the correlations between rate constants and monomer structures can be discussed. It seems that the Taft polar and steric substituent constants, σ^* and E_s , are most adequate to characterize the electronic and spatial natures of ester groups.^{9,10} Substituent constants for the ten ester groups studied are collected in Table V, a part of which is estimated as indicated.

TABLE V
 Taft Substituent Constants for the Ester Groups

Ester group	σ^* ^a	E_s ^b
Isopropyl	-0.190	-0.47
Ethyl	-0.100	-0.07
β -Cyclohexylethyl	-0.02 ^c	
Methyl	0.00	0.00
γ -Phenylpropyl	0.020	-0.45
β -Phenylethyl	0.080	-0.43
β -Methoxyethyl	0.19 ^c	-0.77
Benzyl	0.215	-0.38
β -Chloroethyl	0.385	-0.90
Phenyl	0.600	-0.90

^a Data of Taft.⁹^b Data of Taft.¹⁰^c Estimated as $\sigma^*/2.8$ for the XCH_2 group.¹¹

Rate of Propagation

Propagation rate constants k_p are plotted against σ^* values in Figure 6. In spite of inevitable experimental errors in obtaining individual k_p as estimated in the Results section, we find an essential increase of k_p as σ^* becomes larger with a correlation coefficient of 0.99. In other words, the monomer with the stronger electron-attracting ester group tends to propagate with greater ease. β -Cyclohexylethyl and benzyl monomers show extraordinarily large k_p . These monomers will be discussed later and are omitted as exceptions in the following analysis. Application of the method of regression analysis gives slope = $+0.70 \pm 0.18$ at the level of 95% confidence. The scatterings of individual determinations as in Figures 1-5 reflect an inaccuracy of the slope of ± 0.18 . The estimation of experimental errors up to $\pm 40\%$ in the Results section is apparently too large. The absence of any steric effect of ester groups on k_p is clear from Figure 7, where the benzyl monomer is again an exception. (The E_s value for the β -cyclohexylethyl group is not known.) Hence the Taft-Ingold or the Taft equation

$$\log (k/k_0) = \rho^* \sigma^* + \delta E_s \quad (7)$$

for the present reaction reduces to

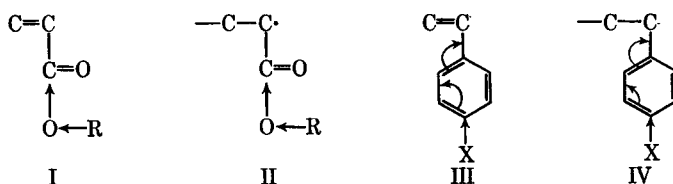
$$\log k_p = 0.70 \sigma^* + 2.2 \quad (8)$$

Burnett et al.¹² and Grant and Grassie¹³ concluded that k_p values remained virtually constant and independent of the ester groups from their experiments on methyl, *n*-propyl, *n*-butyl, and *tert*-butyl methacrylates. The apparent disagreement with our conclusion unquestionably comes from the difference in the range of polar character of ester groups examined.

Imoto et al.¹ obtained a similar relationship for a series of *p*-substituted styrenes, where

$$\log k_{pX}/\log k_{pH} = +0.6\sigma \quad (9)$$

and X = *p*-methoxy, *p*-methyl, *p*-fluoro, *p*-chloro, *p*-bromo, *p*-cyano, and hydrogen. It is interesting to note that in the present methacrylate system, there is no direct conjugation between a vinyl group or unpaired electron and ester group R, (I and II), whereas there is in the styrene



system, (III and IV), and that the reaction constant ρ^* for the present nonconjugative system is not smaller than that for a conjugative styrene system.

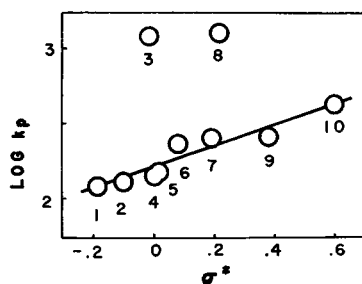


Fig. 6. Taft correlation between $\log k_p$ and σ^* of ester groups: (1) isopropyl; (2) ethyl; (3) β -cyclohexylethyl; (4) methyl; (5) γ -phenylpropyl; (6) β -phenylethyl; (7) β -methoxyethyl; (8) benzyl; (9) β -chloroethyl; (10) phenyl.

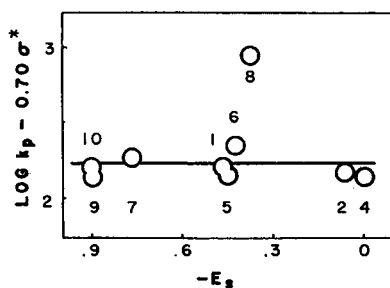


Fig. 7. Taft correlation between $\log k_p - 0.70\sigma^*$ and E_s of ester groups. (1)-(10) as in Fig. 6.

Ötsu et al.¹⁴ studied the relative reactivities ($1/r_1$) of methacrylate monomers towards the polystyrene radical and established the Taft equation,

$$\log 1/r_1 = +0.33\sigma^* + \text{constant} \quad (10)$$

Similar correlation of the relative reactivities of methacrylates towards the poly(methyl methacrylate) radical from the data reported by Bevington and Malpass,¹⁵ by Ōtsu et al.,¹⁶ and by Yokota and Ishii¹⁷ gives

$$\log 1/r_1 \simeq +0.2\sigma^* + \text{constant} \quad (11)$$

again with a positive slope. These results indicate that a monomer with a stronger electron-attracting ester group is more reactive towards two reference polymer radicals. This was attributed¹⁶ to the larger resonance contribution of such monomers.

Combination of r_2 from such copolymerization studies with k_p from the present study enables us to discuss the relative reactivities (k_{21}) of various polymethacrylate radicals as shown in Table VI.

$$k_{21} = k_p/r_2 \quad (12)$$

TABLE VI

Ester group	Reactivity vs. styrene		Reactivity vs. methyl methacrylate	
	r_2	k_{21} , l./mole-sec.	r_2	k_{21} , l./mole-sec.
Isopropyl	0.74	164	1.20	101
Ethyl	0.41 ^a	308	1.08 ^b	117
Methyl	0.46 ^a	307	1.0	141
β -Phenylethyl	0.51 ^c	443	1.33 ^c	171
β -Methoxyethyl	0.60	415	1.06	235
Benzyl	0.51 ^a	2540	1.05 ^b	1190
β -Chloroethyl	0.46 ^d	552	1.13 ^d	225
Phenyl	0.60 ^a	685	1.72 ^b	239

^a Data of Ōtsu et al.¹⁴

^b Data of Bevington and Malpass.¹⁵

^c Data of Yokota and Ishii.¹⁷

^d Data of Ōtsu et al.¹⁶

The difference of reaction temperature (60°C. for copolymerization and 30°C. for homopolymerization) is not considered. Figure 8 shows the correlations of such reactivities with σ^* values of ester groups towards styrene and methyl methacrylate. The slopes, i.e., the reaction constant ρ^* , were calculated as 0.68 ± 0.25 for styrene and 0.48 ± 0.30 for methyl

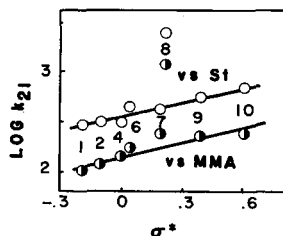


Fig. 8. Taft correlations of polymer radical reactivities and σ^* of ester groups: (O) reactivity vs. styrene; (●) reactivity vs. methyl methacrylate; (1)–(10) as in Fig. 6.

methacrylate. We can safely conclude that a polymethacrylate radical with a stronger electron-attracting ester group is more reactive towards the both reference monomers of opposite polar characters and that the more reactive monomer gives rise to the more reactive polymer radical, contrary to the general picture in vinyl polymerization. The explanation of reactivities based on the resonance contribution is invalidated and the polar contribution should be important, although the precise scheme is not clear. It should be noted that the sum of σ^* in eq. (11) and that from Figure 8 (0.48 ± 0.30) is roughly equal to σ^* in eq. (8).

Rate of Termination

Unlike the k_p values above discussed, termination rate constants $2k_t$ can not be arranged according to the polar character of ester groups. As to the theory of the rate of termination reaction of vinyl radical polymerization, the most plausible may be the diffusion-controlled mechanism developed by North.¹⁸ According to this theory, the termination process consists of three stages; the first stage is a translational diffusion of two polymer radicals to a proximity, the second, concluded by North to be rate-determining, is a segmental diffusion of both chains, and the third is a chemical interaction between two radicals to produce one or two inactive polymer chains. Ōtsu et al.¹⁹ reported a linear correlation between $k_p/k_t^{1/2}$

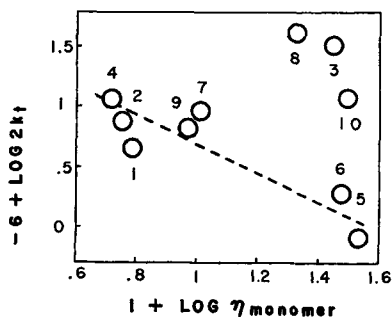


Fig. 9. Correlation between termination rate constant $2k_t$ and monomer viscosity.

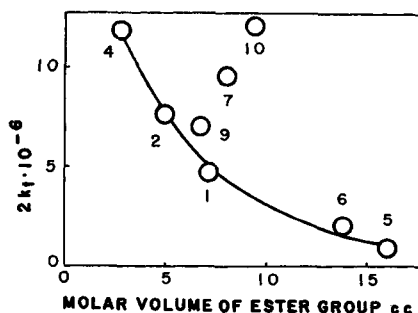


Fig. 10. Correlation of termination rate constant $2k_t$ and molar volume of ester group.

and reciprocals of viscosities of eleven alkyl methacrylates. Now it is possible to discuss $2k_t$ directly instead of the complex $k_p/k_t^{1/2}$. In Figure 9, $2k_t$ and η_{monomer} are plotted in logarithmic scale. It is necessary to omit as before the points for the β -cyclohexylethyl and benzyl esters as well as the point (10) for the phenyl ester, which is only one phenolic ester, to find a rough correlation. In addition, when $2k_t$ and molar volumes of ester groups are plotted in Figure 10, an inversely proportional relationship is observed.* North²⁰ showed that the rate of termination should be inversely proportional to the macroscopic viscosity of the system and to the square root of some characteristic segmental chain length. Here the involvements of monomer viscosity and steric factor of the side chain are meaningful, although the correlation is yet unsatisfactory.

Rate of Initiation

Because of the difficulties in obtaining the rate of initiation R_i , it is difficult to correlate it with structure. In Table III, R_i is transformed into the more straightforward quantity f , initiation efficiency by using the relation

$$R_i = 2k_d f [I] \quad (13)$$

with $k_d = 1.31 \times 10^{-7}/\text{sec.}$ at 30°C. , as calculated by the equation of Van Hook and Tobolsky.²¹ With few exceptions, f values fall in the range of 0.5–0.8. Points (3) and (8), which showed extraordinarily large k_p , are again exceptions and show small f . It is conceivable for these anomalies that some transfer reactions might be involved; (3) β -cyclohexylethyl has tertiary hydrogen and benzyl has a benzylic hydrogen. But, this is puzzling, as some of other monomers also have such active and easily abstractable hydrogens. Moreover, the monomers which show anomalous behavior exhibit regular kinetics as described before. Monomer reactivities in copolymerizations and tacticities of polymers²² are also regular. Further investigations are necessary to clarify this.

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* For the deviation of point (7), a transfer reaction to the ether methylene group may be involved. Rate dependence on initiator concentration is slightly smaller than unity.

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