THE POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF A NITRIC ESTER

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The rates of thermal polymerization of methyl methacrylate have been measured dilatometrically at 25° , 60° , 80° and 90° C, in both the absence and presence of ethylene glycol dinitrate. A kinetic analysis of the results provides direct evidence that the primary step in the thermal decomposition of ethylene glycol dinitrate yields free radicals capable of initiating polymerization of the monomer. The activation energy and rate constant for this decomposition are shown to be given by

 $k_d = 10^{16 \cdot 1} \exp(-39,700/RT) \sec^{-1}$

in the temperature range 60°-90° C.

Consideration of the variation of the molecular weights of the polymers produced with changes in the composition of the system and the concentration of a conventional initiator [2:2'-azo-*bis*-(*iso*butyronitrile)] indicates that chain transfer to the nitric ester is of the same order as that to the monomer. However, there is considerable chain transfer to the azo-initiator when ethylene glycol dinitrate is present.

In the presence of a suitable polymerization initiator the kinetics of thermal polymerization of pure methyl methacrylate in the liquid phase are reproducible, and much work has been done in this field.¹, ², ³, ⁴ Comparatively little published data exist on the kinetics of thermal polymerization in the presence of inert diluents, and it is only recently that such systems have been analysed critically.⁵ A considerable degree of discord is apparent regarding the kinetic effect of the solvent on the polymerization of methyl methacrylate ⁵, ⁶, ⁷ especially with peroxide-type initiators.

This paper describes the application of standard polymerization techniques to the system, methyl methacrylate + ethylene glycol dinitrate, the results providing the first direct evidence that the primary step in the thermal decomposition of this nitric ester involves the production of free radicals capable of initiating polymerization of the monomer. The results obtained by Rogovin and Tsaplina ⁸ for the similar system, methyl methacrylate + glyceryl trinitrate, are shown to be capable of interpretation on the same basis.

Since each solvent radical effects the polymerization of thousands of monomer units, the technique described may be used as a sensitive method of measuring the rate of thermal decomposition of liquid nitric esters, at temperatures only slightly above room temperature and in low concentration. In this way, the rate coefficient and activation energy for the primary step in the decomposition of ethylene glycol dinitrate have been determined.

EXPERIMENTAL

MATERIALS.—*Methyl methacrylate.*—Commercial monomer was washed successively with 10 % sodium hydroxide solution and distilled water to remove the inhibitor. After standing over fused calcium chloride for 2 h and over anhydrous sodium sulphate for a similar period, the monomer was fractionally distilled under reduced pressure. The middle fraction, boiling at 40° C, 80 mm Hg, was stored at 0° C until required.

Ethylene glycol dinitrate.—Available supplies required only filtration. Analysis indicated a nitrogen content of $18\cdot1$ % (theoretical value $18\cdot4$ %) and a water content of $0\cdot18$ %.

2: 2'-azo-bis(isobutyronitrile).—This compound, which decomposes thermally into free 2-cyano-2-propyl radicals by a purely first-order mechanism,⁹ was used as a polymerization initiator. It was obtained from Genatosan Ltd., and recrystallized twice from ethanol (m.p. 102° C).

RATES OF POLYMERIZATION

The rates of thermal polymerization of methyl methacrylate were measured dilatometrically. The monomer and polymer density data of Schulz and Harborth¹⁰ were used in the calculations. Dilatometers of approximately 1 ml capacity were used, and the capillary internal diameter, of approximately 1.5 mm, was determined accurately by mercury calibration.

As is usual in vinyl-type polymerizations, it was necessary to exclude oxygen from the system in order to obtain reproducible rates. This was achieved by filling the dilatometers in an atmosphere of oxygen-free nitrogen; the presence of ethylene glycol dinitrate made the usual freezing and degassing technique inadvisable. After filling a dilatometer with the required amounts of nitric ester + monomer mixture and polymerization initiator, it was sealed at its upper end with a greaseless B.10 cone and socket, surrounded by a mercury seal to prevent ingress of air or water.

The polymerizations were carried out in a water thermostat with glass windows. Temperatures were regulated to within $\pm 0.02^{\circ}$ C of the required value, over the range 20-90° C. Rates of polymerization were essentially constant over the first 10 % conversion and these initial rates are used in all calculations.

VISCOSITY MEASUREMENTS

The chain transfer reactivity of each component in the nitric ester + monomer + initiator system towards a polymer radical was evaluated by measuring the variation of polymer molecular weights with initiator concentration and composition of the system.

Mixtures of ethylene glycol dinitrate (S) and methyl methacrylate (M) with [S]/[M] mole ratios of 0 (pure monomer), 0.073, 1.535 and 5.91 were polymerized at 60° C, in the presence of initiator concentrations varying from 0.4.67 g/l. After 10 % polymerization the polymer was precipitated in a large excess of cold methanol. It was then filtered off, dissolved in chloroform, reprecipitated and dried under reduced pressure at 100° C.

The intrinsic viscosity of each polymer was obtained by determining the specific viscosities of solutions of polymer in freshly distilled chloroform. All solutions were filtered through a fine sintered-glass funnel. A type 1 Ostwald viscometer was employed, the times of flow being measured at $20^{\circ} \text{ C} \pm 0.02^{\circ} \text{ C}$. Polymer concentrations were calculated from the known dilutions of the original solution (approximately 1 %); they were checked by evaporation to dryness of 10 ml of each solution in a weighed vessel, correcting the weight of polymer for a 6 % residual solvent content.

The chain length (\overline{DP}) of polymethyl methacrylate in chloroform solution at 20° C has been shown ^{11, 12} to be related to the intrinsic viscosity $[\eta]$ of the solution by

$$\overline{DP} = 1.81 \times 10^3 \, [\eta]^{1.22}$$

and this relationship has been used to calculate the polymer chain lengths.

RESULTS AND DISCUSSION

The dependence of the rate of polymerization of methyl methacrylate at 60° C on the concentration of 2:2'-azo-*bis*-(*iso*butyronitrile) was determined, both in the absence and presence of ethylene glycol dinitrate. The experimental results are summarized in fig. 1.

In the absence of the nitric ester, the results were found to be in good agreement with the results of Baysal and Tobolsky ¹³ for the same system. If R_t is the thermal rate of polymerization in the absence of a conventional initiator, M the monomer

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concentration and C the concentration of added initiator, then the assumption of a bimolecular termination mechanism leads to the theoretical relationship.

$$R^2 = R_t^2 + K_m^2 M^2 C. (1)$$

In the present work, this equation was found to hold exactly for rates of polymerization up to 20 % per hour at least. The constant in eqn. (1) had the value $K_m = 3.45 \times 10^{-4} \, \text{l.}^{\frac{1}{2}} \, \text{mole}^{-\frac{1}{2}} \, \text{sec.}$



 $\Delta S = 0, M = 8.96$ mole/l., • S/M = 1.535 mole/l.

 $\Box S/M = 0.073$ mole/l.

 $\bigcirc S/M = 5.91$ mole/l.

In the presence of ethylene glycol dinitrate, the dependence of the rate on the initiator concentration was found to be a function of the composition of the system. It may be seen from fig. 1 that the slope K^2 of each line varies with the ratio of nitric ester to monomer; the actual values of K are summarized in table 1. From

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 $C \ge 10^3$, mole 1.

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М	K	$B = K/K_m$	
mole l. ⁻¹	$1.\frac{1}{2}$. mole $-\frac{1}{2}$ sec -1		
8.96	$3.45 \times 10^{-4} = K_m$	1	
8.38	$6.50 imes10^{-4}$	1.9	
3.64	$1.27 imes10^{-3}$	3.7	
1.35	$4\cdot 56 imes 10^{-3}$	13-2	
	<i>M</i> mole 1. ⁻¹ 8·96 8·38 3·64 1·35	M K mole 1. ⁻¹ 1. ^{1/2} . mole ^{-1/2} sec ⁻¹ 8.96 $3.45 \times 10^{-4} = K_m$ 8.38 6.50×10^{-4} 3.64 1.27×10^{-3} 1.35 4.56×10^{-3}	

a simple kinetic analysis of this system, given later, K_m is compounded of rate coefficients for propagation k_p , termination k_t , and thermal decomposition of initiator k_i ,

$$K_m = k_p k_i^{\frac{1}{2}} / k_i^{\frac{1}{2}}$$

Both k_p and k_t are independent of monomer concentration, at low conversions to polymer, and it has been shown also that dilution of methyl methacrylate does not affect the efficiency of initiation by radicals from 2 : 2'-azo-bis(isobutyronitrile).14 Thus, K_m would be expected to be independent of monomer concentration.

The explanation of the unexpected variation in the value of K_m almost certainly lies in the fact that the value of k_t is decreased due to a "bad solvent" effect of

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<u>x²-R</u>², x 10⁵

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the ethylene glycol dinitrate upon the polymethyl methacrylate.¹⁵ In effect, the termination reaction in the system under consideration is diffusion-controlled from the start; the activation energies obtained lend support to this idea. Some experimental evidence for these views was obtained by Burnett and Melville,¹⁶ who measured the individual rate coefficients for the comparable system, vinyl acetate in *n*-hexane, and found that, whereas k_p remained constant, k_t decreased by a factor of 5. It should be noted that if the apparent increase in the value of K_m with concentration of nitric ester were due to enhanced initiation through complex formation between initiator and nitric ester then the values of K should be proportional to some integral power of S; this is not the case. Henceforth, the ratio of the rate of polymerization in the presence of ethylene glycol dinitrate to the rate at equivalent concentrations of monomer and azo-initiator in a "good" solvent, viz. pure methyl methacrylate, is designated B, the " bad solvent " factor (table 1).

The rates of thermal polymerization in the *absence* of added initiator were measured at four temperatures, and with different [nitric ester]/[monomer] ratios. Table 2 summarizes the experimental rates (in mole $1.^{-1} \sec^{-1}$). The parenthetical values are calculated rates, derived from the rates in the absence of nitric ester (S/M = 0) on the assumption that the thermal rate depends on the square of the monomer concentration. It is seen from table 2 that the actual rates of polymerization were much faster than the calculated values. In the particular case where S/M = 5.91, the rate at 60° C was nearly 600 times faster than expected.

TABLE 2

T °C	$S/M \rightarrow 0$	S/M = 0.073	S/M = 1.525	SIM - 5.01
1, C	3/14 = 0	3/M = 0.013	3/m = 1.335	3/14 5.91
25	6.6×10^{-7}	$1.95 imes10^{-6}$	$8.7 imes10^{-6}$	
		(5·31 × 10 ⁻⁷)	(1·1 × 10 ^{−7})	
60	$5{\cdot}48 imes10^{-6}$	$2.86 imes 10^{-5}$	$7.78 imes10^{-5}$	$7.28 imes10^{-5}$
		(4·79 × 10⁻6)	(9·04 × 10 ^{−7})	(1.24×10^{-7})
80	$5.70 imes10^{-5}$	$2\cdot15 imes10^{-4}$	$3.75 imes10^{-4}$	
		$(4.91 imes 10^{-5})$	(9·5 × 10−6)	
90	$2\cdot 39 imes 10^{-4}$	$5.70 imes10^{-4}$	$8\cdot1 imes10^{-4}$	
		(2·08 $ imes$ 10 ⁻⁴)	$(4\cdot02 imes10^{-5})$	

These results led to the suspicion that the ethylene glycol dinitrate was in some way initiating the polymerization of methyl methacrylate. Calculation showed that the large discrepancies in rate could be explained readily on the basis of each decomposing nitric ester molecule providing two free radicals capable of initiating a polymerization chain process. The rate coefficient of decomposition of ethylene glycol dinitrate obtained by Phillips ¹⁷ was used in these calculations, and the assumption was made that the "bad solvent" factor *B*, was the same, for a given S/M ratio, as that determined experimentally in the presence of azo-initiator.

KINETIC SCHEME

In the absence of solvent effects, and ignoring chain transfer, the kinetic scheme is :

initiation	thermal	V_i	
	azo-initiator	$C \rightarrow P_1$	k _i
	propagation	$\mathbf{P}_n + \mathbf{M} \rightarrow \mathbf{P}_{n+1}$	k _p
	termination	$\mathbf{P}_n + \mathbf{P}_m \rightarrow \mathbf{D}$	k _t

where P_r refers to a polymer radical of chain length r, and D any "dead" polymer. From these simple mechanisms, it is easy to show that, in the stationary state, the overall rate R of polymerization is defined by

$$R^2 = R_t^2 + K_m^2 M^2 C, (1)$$

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where $R_t = k_p V_i^{\frac{1}{2}} M k_t^{-\frac{1}{2}}$ = pure thermal rate in the absence of any added initiator, and

$$K_m = k_p k_i^{\frac{1}{2}} k_t^{-\frac{1}{2}}.$$

When solvent is present and acts as an inert diluent, then both R and R_t need to be multiplied by a factor B, the "bad solvent" factor referred to previously. The value of B will depend, of course, on the ratio of solvent to monomer (S/M)in the system under consideration. In a pure methyl methacrylate system B is assumed to have the value of unity.

In the present system, the solvent decomposes thermally to free radicals which are capable of initiating polymerization of the monomer. Assuming that each molecule of ethylene glycol dinitrate yields two such radicals in the primary decomposition step,

$$S \rightarrow 2P_1, \quad k_d$$

then the complete rate expression becomes

$$R = Bk_{n}M(V_{i} + k_{i}C + 2k_{d}S)^{\frac{1}{2}}k^{-\frac{1}{2}}.$$
 (2)

In the absence of the 2: 2'-azo-bis(isobutyronitrile) initiator, this can be written as

$$R^2 = B^2 R_t^2 + 2B^2 k_p^2 k_d M^2 S k_t^{-1}.$$
 (3)

Two assumptions in the above analysis merit consideration at this point. In the derivation of eqn. (1) it has been assumed that the polymerization of methyl methacrylate in solution follows a first-order relationship with respect to monomer, over the range of concentrations used in this work. This has been substantiated in benzene solutions, by the work of Schulz and Harborth,¹ Smets ⁷ and Burnett and Loan.⁵ The last named found a trend towards higher order only at monomer concentrations less than 20 %. In cases where the monomer yields a propagating radical of greater reactivity than that from methyl methacrylate, e.g. methyl acrylate, vinyl acetate, or where peroxide-type initiators are used, the apparent order varies in a complicated manner with monomer concentration. The same authors found also that, using 2:2' azo-bis(isobutyronitrile) as initiator, the rate of initiation was independent of monomer concentration. This, in fact, is the second assumption made in the above analysis. When benzoyl peroxide is used as initiator, Basu, Sen and Palit¹⁸ have shown that initiation is first order with respect to methyl methacrylate.

From eqn. (3) it may be seen that measurements of R and R_t for mixtures of monomer and nitric ester at different temperatures not only test the kinetic analysis but also enable the rate coefficient k_d and activation energy for initial decomposition of the nitric ester to be determined. For the system S/M = 0.073, the following expression was obtained from the results in tables 1 and 2:

$$k_d = 10^{16.1} \exp(-39,700/RT) \sec^{-1}, (60-90^{\circ} \text{ C}).$$

This value is in good agreement with the work of Phillips,¹⁷ in which the rate of evolution of nitrogen dioxide from the liquid nitric ester was measured. Phillips obtained the value $10^{15.6} \exp(-39,000/RT) \sec^{-1}$ for the range $85-105^{\circ}$ C. Table 3 shows the agreement between calculated and observed rates of polymerization for the system S/M = 0.073, using the above value of k_d in eqn. (3).

TABLE 3

Τ°C	R (calc.) mole 1. ⁻¹ sec ⁻¹	R (obs.) mole l. ⁻¹ sec ⁻¹
25	$1.14 imes10^{-6}$	$1.95 imes10^{-6}$
60	$2.79 imes10^{-5}$	$2.86 imes10^{-5}$
80	$2.06 imes10^{-4}$	$2.15 imes 10^{-4}$
90	$5.80 imes10^{-4}$	$5.70 imes10^{-4}$

The agreement leaves little doubt that the thermal decomposition of the ethylene glycol dinitrate was responsible for the greatly enhanced rates of polymerization.

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For the system S/M = 1.535, the activation energy was nearly 6000 cal mole⁻¹, lower than that for the system S/M = 0.073. This is probably because the activation energy for polymer radical termination may no longer be assumed to be negligible. The high apparent figure of nearly 12,000 cal mole⁻¹ is close to the critical increment for diffusive displacement in a liquid polymer, and is thus consistent with the considerable degree of aggregation of polymer chains that must occur in a system containing 70 % " bad solvent ".

It is possible to give a quantitative explanation of the results of Rogovin and Tsaplina ⁸ for the glyceryl trinitrate + methyl methacrylate system on the basis of the foregoing analysis. The rate coefficient for initial thermal breakdown of glyceryl trinitrate may be taken as $1.53 \times 10^{-7} \sec^{-1}$ at 100° C, from the work of Phillips.¹⁷ In table 4 the experimental results of Rogovin and Tsaplina have been averaged, for purposes of comparison with the values calculated from eqn. (3). Again, the good agreement indicates that nitroglycerin resembles ethylene glycol dinitrate in its ability to initiate methacrylate polymerization by a free-radical mechanism.

		TABLE 4	
% nitroglycerin	rate	rate (calc.)	
	%/h	mole $1.^{-1}$ sec ⁻¹	mole l. ⁻¹ sec ⁻¹
	11.1	$2.62 imes10^{-4}$	$2.62 imes10^{-4}$
1	19.7	$4.65 imes10^{-4}$	5.9×10^{-4}
5	39.9	9.4 $ imes$ 10 ⁻⁴	9.7 $ imes$ 10–4
10	56.8	$1.34 imes10^{-3}$	$1.28 imes10^{-3}$
20	90.6	$2.0 imes 10^{-3}$	1.7×10^{-3}

CHAIN TRANSFER AND MOLECULAR WEIGHTS

The three transfer mechanisms by which the molecular weight of the polymer may be reduced involve the monomer (k_f) , the ethylene glycol dinitrate $(k_{f'})$, and the 2: 2'-azo-bis(isobutyronitrile) (k_c) ; transfer to "dead" polymer may be neglected for the relatively unreactive polymethyl methacrylate radical at low conversions. From the given kinetic analysis, the average chain length \overline{DP} of the polymer can be shown to be:

$$\overline{DP}^{-1} = \frac{k_i^{\frac{1}{2}} (k_i C + 2k_d S + V_i)^{\frac{1}{2}}}{Bk_p M} + \frac{k_f}{k_p} + \frac{k_f'}{k_p} \frac{S}{M} + \frac{k_c}{k_p} \frac{C}{M}.$$
 (4)

The experimental points in fig. 2 show how the viscosity average chain lengths of the polymers varied with the composition of the nitric ester + monomer system and the concentration of azo-initiator used in their preparation. Also included, for comparison, are the experimental results of Baysal and Tobolsky ¹³ who polymerized methyl methacrylate at 60° C with the same azo-initiator, but in the absence of ethylene glycol dinitrate. From the latter results, the value of the transfer constant k_f/k_p for monomer is given by the intercept, viz. 3.0×10^{-5} and this value has been used in evaluating the remaining transfer constants. The same results indicate that the transfer constant for initiator is low (approximately 6×10^{-3}).

The results for the nitric ester + monomer system where S/M = 1.535 lead to an intercept of 1.0×10^{-4} , which from eqn. (4) is equal to

$$\frac{k_t^{\frac{1}{2}}(2k_dS+k_0M^2)^{\frac{1}{2}}}{Bk_pM}+\frac{k_f}{k_p}+\frac{k_f'}{k_p}\frac{S}{M}.$$

Assuming the approximate values $k_p/k_t^{\frac{1}{2}} = 0.118$, $k_d = 1.6 \times 10^{-10}$ and $k_0 = 1.1 \times 10^{-12}$, the first term in this expression has a value of 2.5×10^{-5} . Thus,

$$rac{k_f}{k_p} + rac{k_f'}{k_p}rac{S}{M} = 7.5 imes 10^{-5}, \ k_f'/k_p = 3 imes 10^{-5}.$$

and

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Chain transfer by polymethyl methacrylate radicals to ethylene glycol dinitrate is small, being of the same order as that to monomer.

Where transfer to azo-initiator may be neglected, it may be seen from eqn. (4) that a plot of \overline{DP}^{-1} against $C^{\frac{1}{2}}$ is linear. However, it is apparent from fig. 2 that this is not the case for the present system. Using the transfer constants



FIG. 2.—Variation of viscosity average chain length DP with initiator concentration and mole ratio of ethylene glycol dinitrate (S) to methyl methacrylate (M); 60 ° C.

- $\triangle S = 0, M = 8.96$ mole/l.
- S/M = 1.535 mole/l.
- $\Box S/M = 0.073$ mole/l.
- $\bigcirc S/M = 5.91$ mole/l.

already derived, the following equation was found to fit the experimental points for the three systems under consideration:

$$\overline{DP}^{-1} = AC^{\frac{1}{2}} + 3 \times 10^{-5} (S/M) + 0.12(C/M) + 3 \times 10^{-5}.$$
 (5)

This equation has been used to derive the curves shown in fig. 2. The values of A in eqn. (5) were calculated from the observed rates of polymerization, depending as they do on the values of B and M; these values are:

$A = 1.60 \times$	10-3 l. [‡]	mole-1	for	the system	S/M	= 0.073
$= 1.84 \times$	10-3	,,	,,	,,	,,	= 1.535
$=$ 1·39 \times	10-3	,,	,,	,,	"	= 5.91

and

The transfer constant to initiator,

$$k_c/k_p = 0.12,$$

is approximately twenty times larger than in the pure monomer system, at the same temperature. No explanation can be advanced for this difference, but there is little doubt from the above that 2: 2'-azo-bis(isobutyronitrile) functions as a chain transfer agent to polymethyl methacrylate radicals, in the presence of ethylene glycol dinitrate. In this system the azo-initiator behaves in a similar manner to peroxide-type initiators in methyl methacrylate. Thus, Baysal and Tobolsky 1^3 obtained a transfer constant of 0.33 for cumene hydroperoxide, and

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Basu, Sen and Palit¹⁸ found that although benzoyl peroxide did not undergo transfer, the *p*-nitro-derivative did so when in fairly high concentration. Also Smets and Reiske 19 observed increased chain transfer at high initiator concentrations for methyl methacrylate in dichlorethane solvent.

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