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GRAFT POLYMERISATION OF NATURAL RUBBER

BY

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INTRODUCTION

The properties of natural rubber could be modified by several methods. One could, for example, either change the chemical nature of the rubber molecule or alter its structure. A useful method of modification involves the polymerisation of monomers (particularly vinyl monomers) in the presence of natural rubber. Under suitable conditions, a chemical reaction takes place between the monomer (or polymerising monomer) and the rubber molecule. Graft polymers of natural rubber are then obtained. In graft polymers, secondary polymer chains are attached at various positions to an already existing polymer "backbone", and grafting can result in the establishment of secondary polymer chains containing long sequences of monomers. The properties of graft copolymers may thus be widely different from those of random copolymers which are obtained by the copolymerisation of two monomers. By the selection of suitable monomers and grafting conditions it should be feasible to modify the properties of natural rubber in any desired way.

The most important work on the grafting of monomers to natural rubber has been done at the Natural Rubber Producers' Research Association (NRPRA) in U.K. It has been shown that rubber in all its forms—as latex, in solution and as a solid could be used for this purpose (Bateman, 1963).

The objective of our work was to study broadly the kinetics of the reaction of rubber in latex form (ammonia preserved field latex) with monomers under various conditions. The use of latex for kinetic studies, however, complicates the interpretation of the results. The non hydrocarbon constituents in latex as well as the high viscosity of the medium may affect the rate. Since the reaction system is heterogenous the surface area of the rubber particles, as well as diffusion, may be limiting factors in the kinetics.

Rate of reaction

The rate of reaction was followed by both ultraviolet spectroscopy and gas chromatography. All monomers studied had either conjugated double bonds or auxochromic groups and therefore absorbed in the *u. v.* region. From absorption spectrum studies of known concentrations of monomer λ max was determined for each monomer studied. The rate of reaction of monomer in the presence of rubber latex was then determined by measuring the absorbance (at λ max) of the reaction mixture as a function of time.

In the gas chromatographic studies, the concentration of unreacted monomer in the reaction mixture was obtained by injecting a known amount of the mixture into the gas chromatograph and measuring the peak area. Peak areas were converted into concentrations by comparison with the peak areas of an inert standard (ethyl acetate) added to the reaction mixture. The use of an inert standard of comparison eliminates any errors due to irreproducibility in the sampling and experimental procedures.

In both these methods the decrease in the concentration of monomer as a function of time is obtained directly. This is in contrast to the dilatometric method of analysis used in earlier work where the experimentally measured quantity (decrease in volume) can be converted into rate only with the help of other data.

EXPERIMENTAL

Ultraviolet spectroscopic studies

A diluted solution of ammonia preserved field latex was used in all experiments. Dilution was effected with distilled water made oxygen free by bubbling with nitrogen for one hour. Aqueous solution of initiator (sodium persulphate) and destabilised monomer were added to the diluted latex, and mixed well. The mixture was maintained at the required temperature in a thermostat. Samples were withdrawn at various times, diluted with distilled water, unreacted monomer was extracted with cyclohexane or chloroform and the *u. v.* spectrum was obtained. Concentration of monomer was estimated from the absorbance value. The spectrophotometer used was a Unicam SP 8000.

Gas chromatographic studies

A Perkin Elmer F 11 gas chromatograph equipped with a flame ionisation detector was used. The columns were packed with Apiezon L on chromosorb P (80-100 mesh) and 5.1 silicone gum rubber E-301 on AW-DMcs chromosorb G (80-100 mesh). The carrier gas, a mixture of hydrogen and air, was passed at pressures of 15, 17 and 25 lb in.^{2} respectively. About 0.4 μ l samples of the reaction mixture were withdrawn at various times and injected into the column. The concentration of the monomer was obtained from the peak.

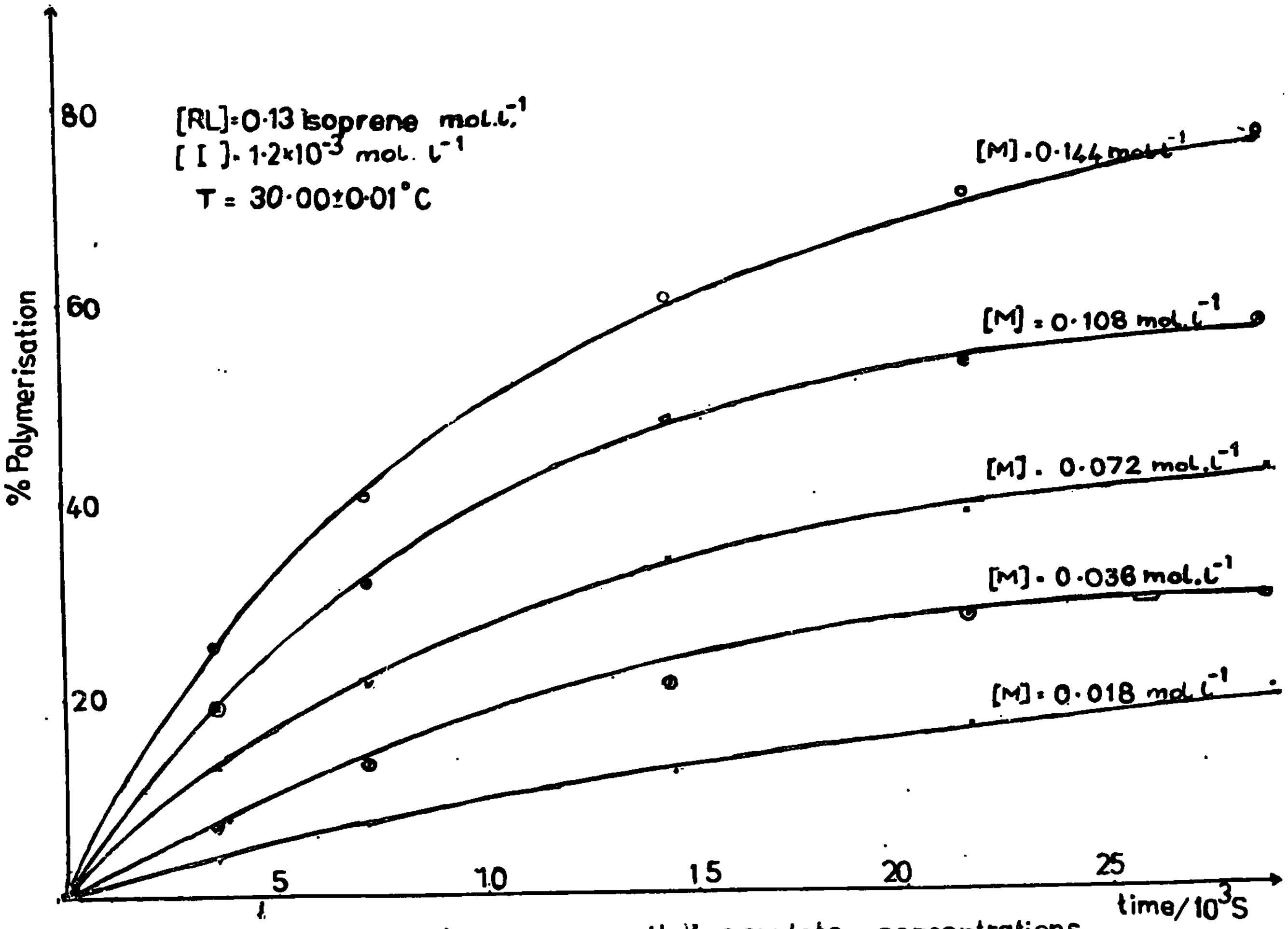
RESULTS

The rate of polymerisation of methyl acrylate, methyl crotonate and methyl methacrylate, in the presence of ammonia preserved field latex, was studied as a function of the concentration of monomer (M), initiator (I) and rubber in latex form (R) at various temperatures. The results obtained have been presented as percentage polymerisation *vs.* time curves.

Effect of monomer concentration

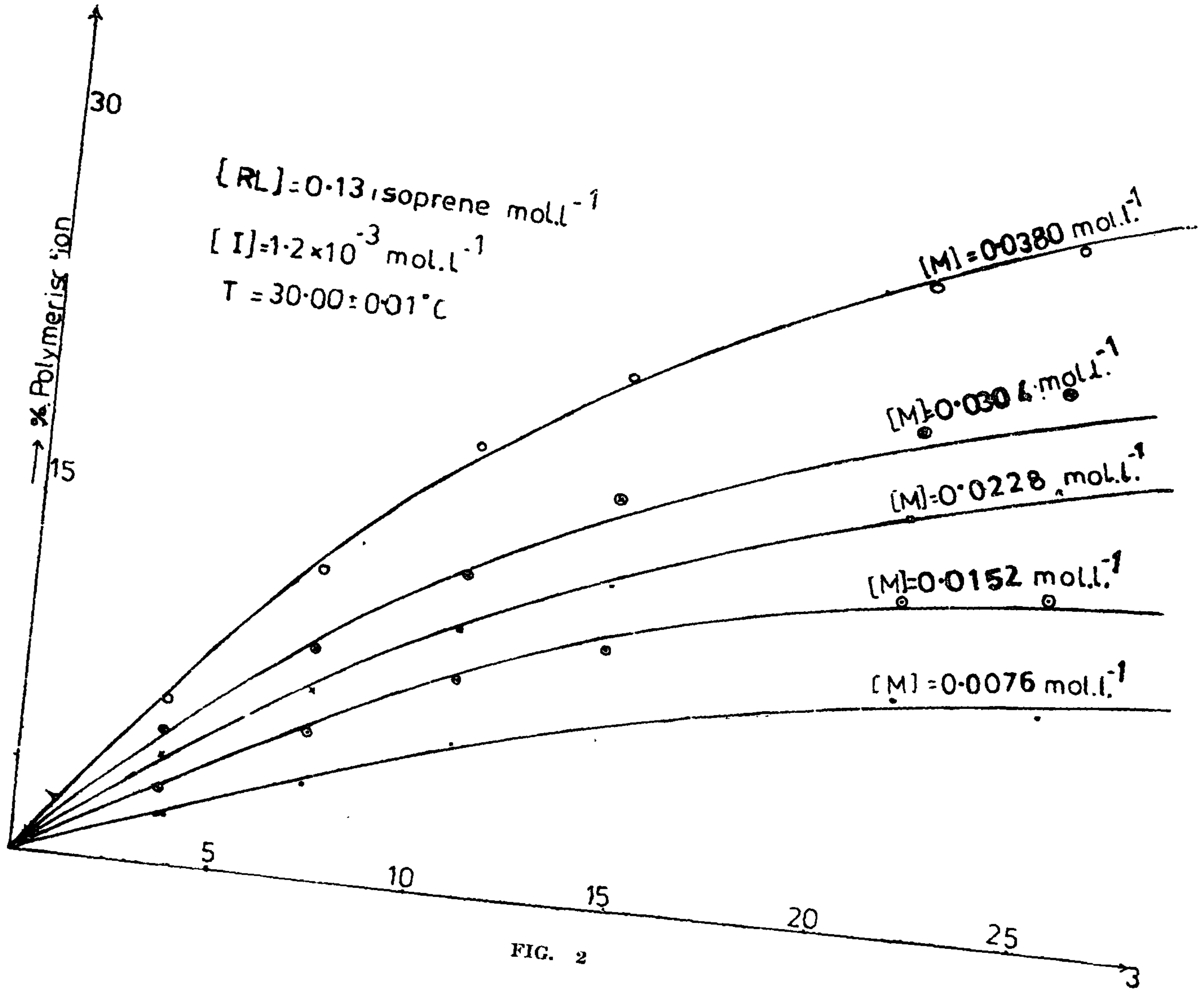
Figs. 1, 2 and 3 show the percentage polymerisation *vs.* time curves for various initial concentrations of methyl acrylate, methyl crotonate and methyl methacrylate respectively. The shapes of the curves are similar in all three cases. The rate decreases rapidly with time. In contrast to graft polymerisation in solution (Bateman, 1963), using oil soluble initiators there is neither an induction period nor an autocatalytic effect.

A plot of the results according to first order kinetics is shown in Fig. 4. It is seen that first order kinetics is obeyed only for the initial 10 to 15% of the reaction. The rate then decreases much too rapidly than that predicted by the first order kinetics. After about 50% reaction (with respect to monomer) the rate becomes very slow. Rate *vs.* percentage conversion plots shown in Fig. 5 brings this out clearly. The rapid fall off in the rate with time (or with percentage polymerisation) for the polymerisation of



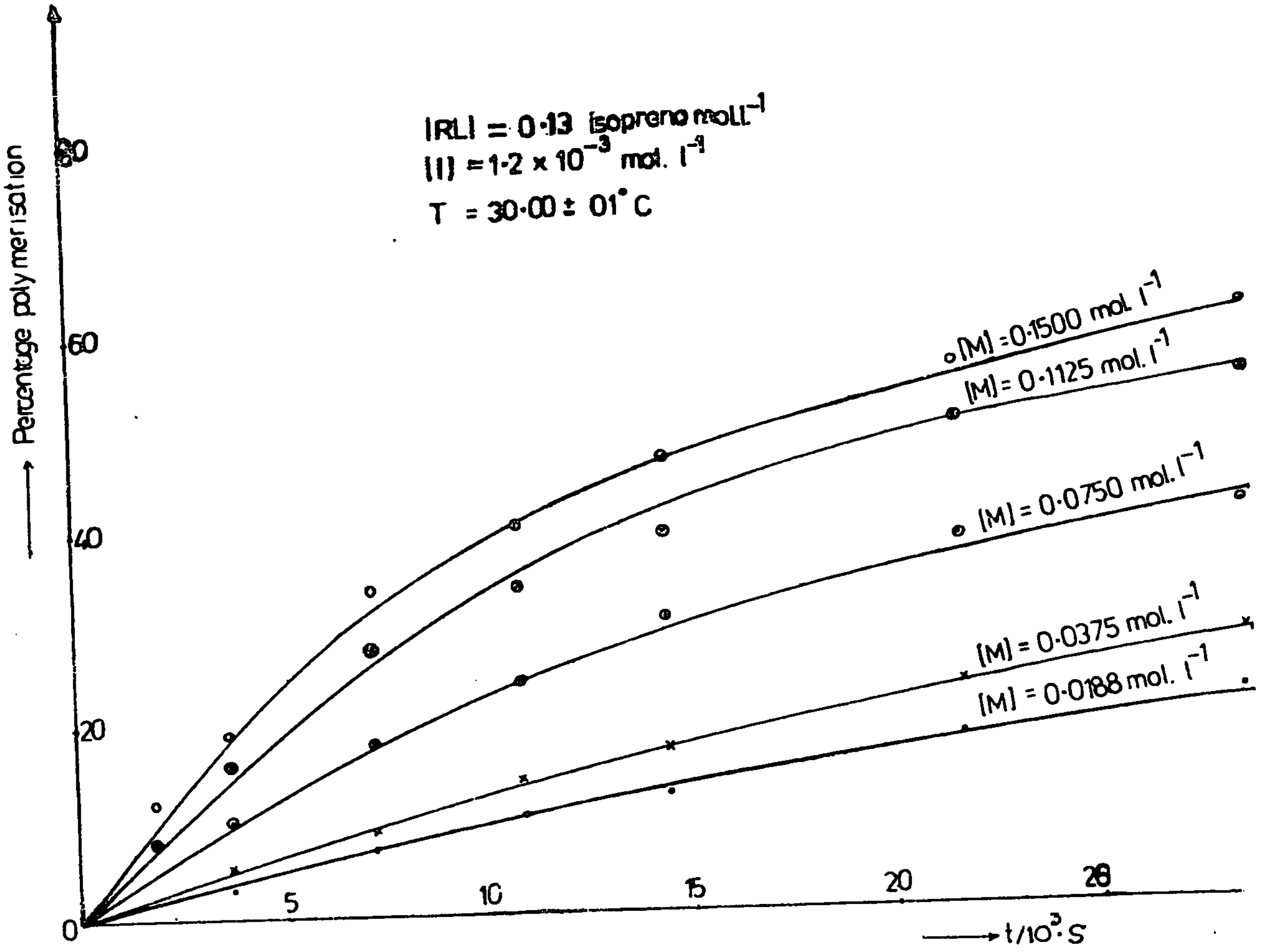
Polymensation curves at various methyl acrylate concentrations

FIG. 1



[RL] = 0·13 isoprene mol.l.$^{-1}$
[I] = 1·2 × 10^{-3} mol.l.$^{-1}$
T = 30·00 ± 0·01 °C
→ % Polymerisation
30
15
[M] = 0·0380 mol.l.$^{-1}$
[M] = 0·0304 mol.l.$^{-1}$
[M] = 0·0228 mol.l.$^{-1}$
[M] = 0·0152 mol.l.$^{-1}$
[M] = 0·0076 mol.l.$^{-1}$
5
10
15
20
25
3

FIG. 2



Polymerisation curves at various methyl methacrylate concentrations.

FIG. 8

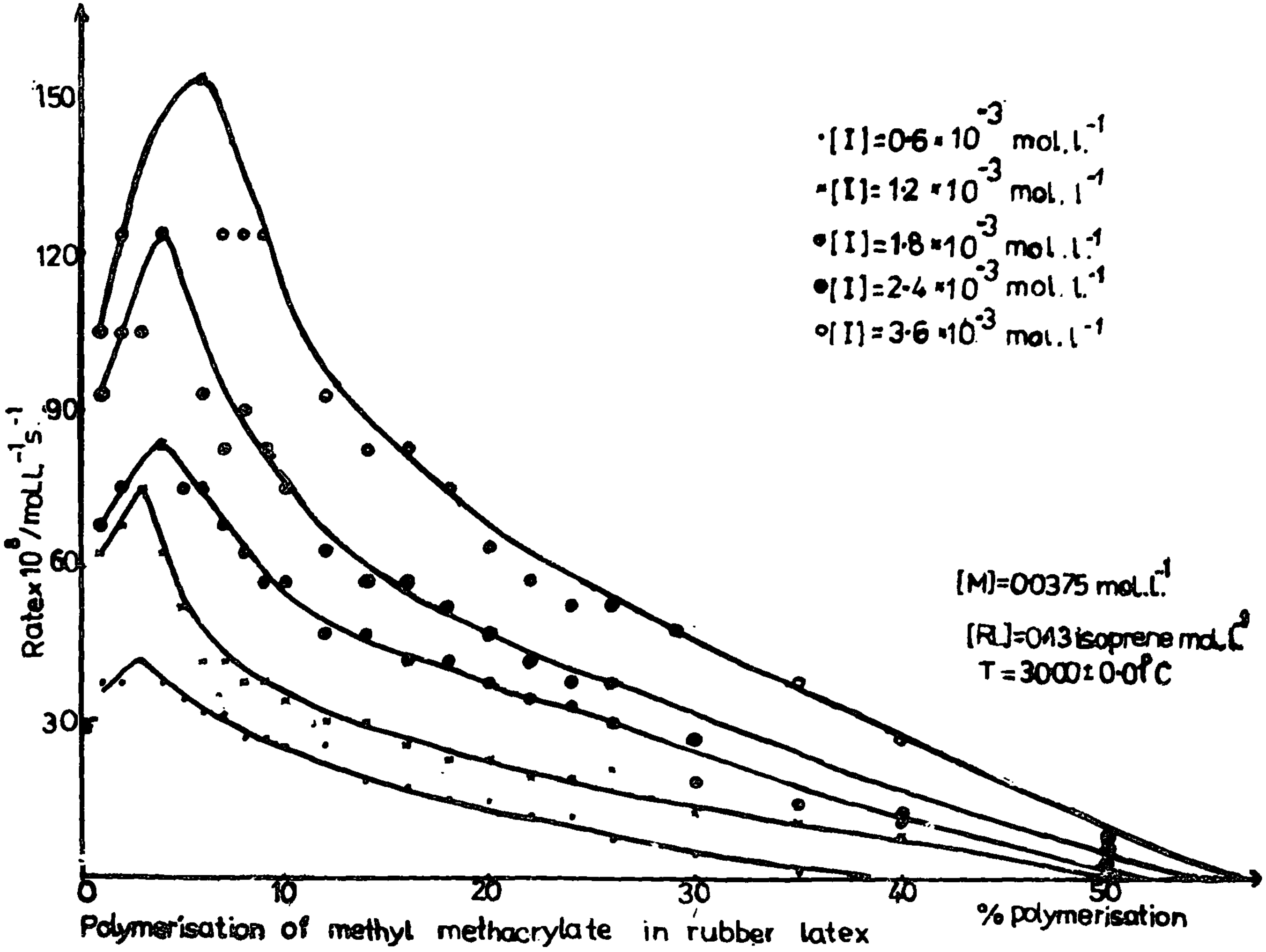
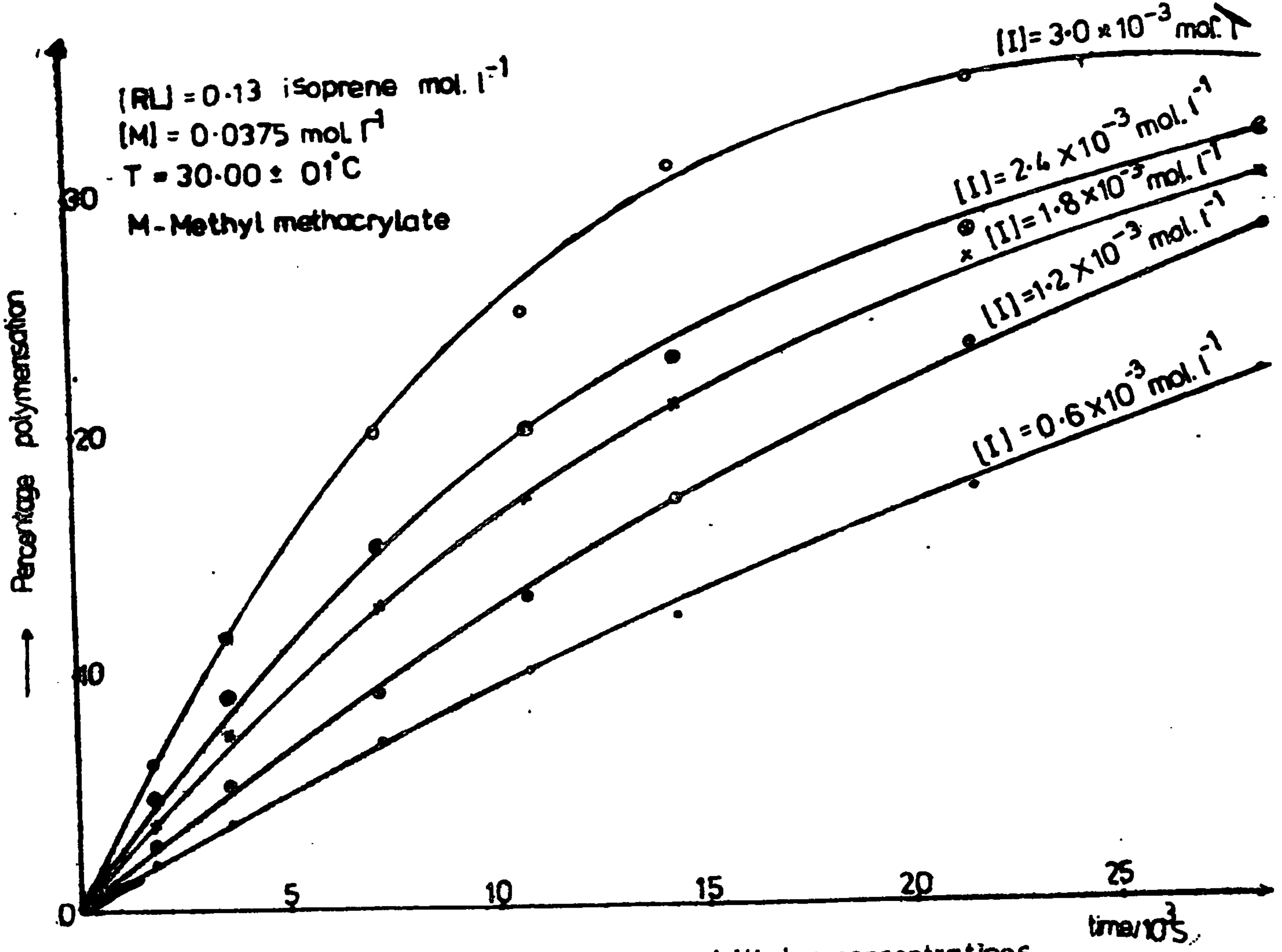

150
120
90
60
30
Rate × 10^8 / mol.L^-1 s^-1
0
10
20
30
40
50
% polymerisation
Polymerisation of methyl methacrylate in rubber latex
· [I] = 0·6 × 10^-3 mol. l.^-1
× [I] = 1·2 × 10^-3 mol. l^-1
⊗ [I] = 1·8 × 10^-3 mol. l.^-1
● [I] = 2·4 × 10^-3 mol. l.^-1
○ [I] = 3·6 × 10^-3 mol. l^-1
[M] = 0·0375 mol. l.^-1
[RL] = 0·13 isoprene mol. l^-1
T = 30·00 ± 0·01°C

FIG. 4



Polymerisation curves at various initiator concentrations

FIG. 5

methyl methacrylate in latex had already been observed by NRPRA. Our results support this work and also show that methyl acrylate and methyl crotonate too show the same behaviour (Bateman, 1963). Further experiments on how the rate *vs.* percentage conversion curve depends on various factors may provide some insight into this rapid fall off in rate.

Since the kinetics becomes more and more complex with time, emphasis was placed on initial rates. The effect of various factors on the rate was studied by changing one variable when all the others were kept constant. Initial rates of various monomer concentrations (in the concentration range 2 to 15×10^{-2} mole l^{-1}) also confirmed that the rate is directly proportional to the monomer concentration.

Effect of initiator concentration

The polymerisation time curves for various initiator concentrations are shown in Fig. 6 for methyl methacrylate. The initiator used was sodium persulphate. The same type of curves were obtained for methyl acrylate and methyl crotonate. In all these cases the initial rates were found to show a half order dependence with initiator concentration at low initiator concentrations (concentration range: 0.3 to 1.8×10^{-3} mole l^{-1}). The order increased as the concentration of the initiator was increased. For example, when the concentration of the initiator was 3×10^{-3} mole l^{-1} the order was found to be about 0.8. Higher concentrations of initiator could not be used since there was then coagulation of rubber.

Effect of concentration of rubber in latex

The rate of reaction was found to increase with increasing concentration of rubber in latex form (R). There was, however, no unique relationship between these two variables. When the concentration of rubber was about 1.0 molar (note: concentrations have been calculated on the basis of *isoprene* units) the exponents in the rate equation was about 0.6. This decreased gradually with increasing concentration of rubber latex and had a value of about 0.3 when the concentration was one molar. Addition of emulsifiers was found to markedly increase the rate of reaction. It appears likely that the increase in rate on the addition of emulsifier is at least partly due to the increase in surface area of the rubber particles.

Effect of temperature

Experiments showed that the rate was not very sensitive to temperature within the temperature studied (30—60 °C). From the experimental initial rates at various temperatures the activation energy E for the reaction was calculated using the Arhenius equation.

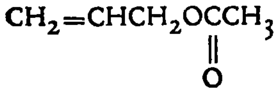
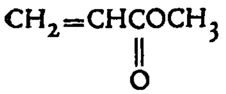
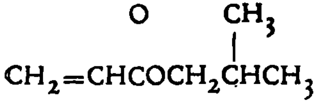
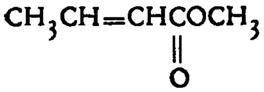
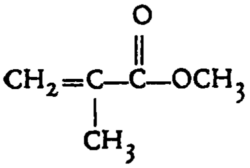
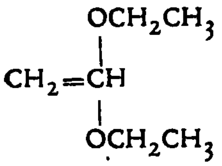
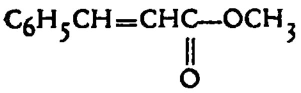
$$k = Ae^{-E/RT}$$

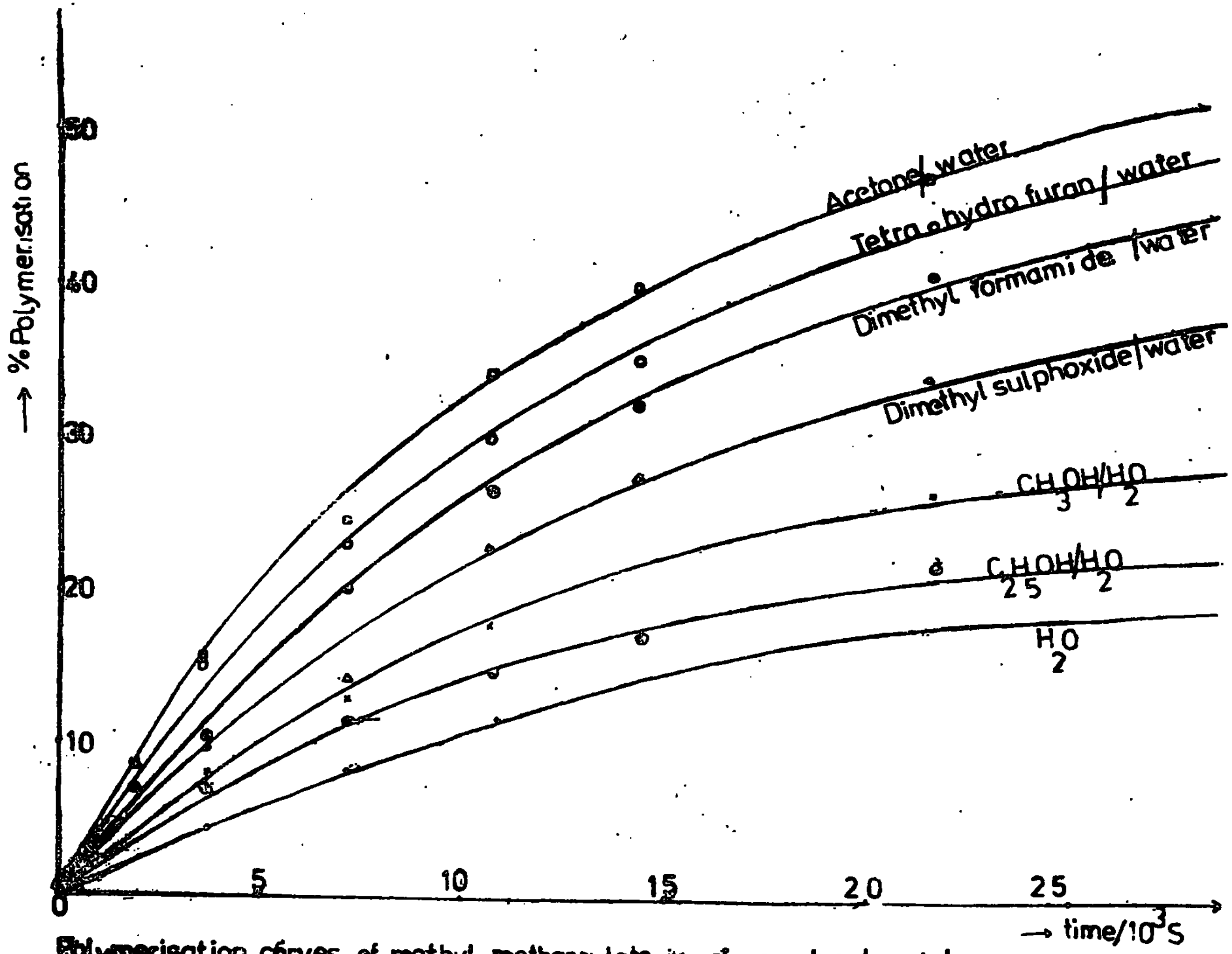
For methyl methacrylate E was about 0.5 kcal mole^{1-}; for methyl acrylate and methyl crotonate E was about 2.0 kcal mole^{-1}. The activation energies are thus low.

Effect of different monomers and different solvents

The relative rates of polymerisation of different monomers in rubber latex are summarised in Table 1. It appears that notwithstanding steric effects electron withdrawing groups decrease the rate of the reaction. The relative rates of polymerisation of methyl methacrylate in some solvent mixtures were also measured; the results are given in Fig. 6. The reaction seems to be faster in dipolar aprotic solvents than in protic solvents.

TABLE I

Monomer	Initial rate of polymerisation $\times 10^7$ mol. l.$^{-1}$ s^{-1}	
$CH_2{=}CHCH_2OH$	Allyl alcohol	29.2
$CH_2{=}CHCH_2OCH_2CH_3$	Allyl ethyl ether	26.0
 $CH_2{=}CHCH_2O\underset{\overset{\|}{O}}{C}CH_3$	Allyl acetate	25.5
 $CH_2{=}CH\underset{\overset{\|}{O}}{C}OCH_3$	Methyl acrylate	21.1
 $CH_2{=}CH\underset{\overset{\|}{O}}{C}OCH_2CH_3$	Ethyl acrylate	20.3
 $CH_2{=}CHCOCH_2\overset{\overset{CH_3}{\vert}}{C}HCH_3$	Iso-butyl acrylate	18.2
 $CH_3CH{=}CH\underset{\overset{\|}{O}}{C}OCH_3$	Methyl crotonate	17.6
$CH_2{=}CHCH_2Cl$	Allyl chloride	14.7
$CH_2{=}CHCH_2Br$	Allyl Bromide	14.1
$CH_2{=}CHCN$	Acrylonitrile	13.3
 $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$	Methyl methacrylate	7.9
 $CH_2{=}\overset{\overset{OCH_2CH_3}{\vert}}{\underset{\underset{OCH_2CH_3}{\vert}}{C}}H$	Acrolein acetal	4.9
 $C_6H_5CH{=}CH\underset{\overset{\|}{O}}{C}{-}OCH_3$	Methyl cinnamate	1.9



Polymerisation curves of methyl methacrylate in various solvent mixtures

FIG. 6

Mechanism of Polymerisation

The main objective of kinetic studies is to deduce the *mechanism* of the reaction, that is to deduce the sequence of steps by which the reactants are converted into products.

There is strong evidence that the polymerisation of vinyl monomers in the presence of rubber latex proceeds by a free radical mechanism. In the simplest possible case a free radical mechanism for the polymerisation of a monomer M involves three steps:— initiation, propagation and termination of free radicals. If it is assumed that the concentration of the propagating free radicals does not change with time (steady state assumption), then it can be shown (Billmeyer, 1971) that the velocity (v) of the reaction is given by the equation

$$v = \frac{-d[M]}{dt} = k_p \left(\frac{fk_d\,[I]}{k_t} \right)^{\frac{1}{2}} [M]$$

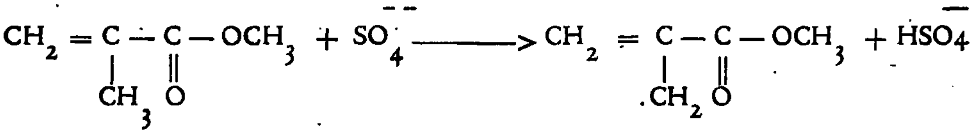
where k_d, k_p and k_t are the rate constants for the initiator decomposition, for the propagation reaction and for the termination reaction, respectively, square brackets [ ] denotes concentrations; f is the fraction of radicals formed from the intiator which initiates chains.

The system under study, in our experiments, is fairly complex. It is heterogeneous (rubber hydrocarbon as emulsion, monomer and persulphate initiator in the aqueous phase) and thus surface area and diffusion phenomena may affect the rate. Furthermore, several types of free radical intermediates are possible and, initiation, propagation and termination reactions may take place by more than one mechanism. For example, the initiator radicals I· (I· $= SO_4^{-}$ in our experiments), formed by the decompositon of initiator (I) could possibly initiate free radicals by reaction both with the monomer (M) and the rubber hydrocarbon (R). These reactions could take place in at least two ways—by addition across a double bond or by abstraction of a hydrogen atom from an active site. It is also possible that free radicals on the rubber hydrocarbon are formed by the reaction of monomer (or polymerising monomer) free radicals with rubber. For the propagation reaction too several possibilities exist. The monomer M may react with polymerising monomer free radicals $M\cdot_n$ (in aqueous phase or in a newly formed homopolymer phase) or with rubber radicals (in rubber phase). Termination reactions may take place by combination of any two of the free radicals present in the system, or by disproportionation of some of the radicals. In addition to initiation, propagation and termination reactions various chain transfer reactions are also possible.

DISCUSSION

The first order dependence of rate on the monomer concentration is consistent with the equation given above for a simple free radical mechanism. The dependence of rate on the *nature* of the monomer suggests that the initiation step involves, at least partially, the reaction between the initiator and monomer. There are two ways in which this reaction can take place—by addition of I· at the double bond or by abstraction of a hydrogen atom from an active centre. It appears from the order of reactivity of monomers that electron withdrawing groups retard the reaction (Table 1). Since the initiator radical is a radical anion (SO_4^{-}) it appears that the *addition* of the initiator radical to monomer is not a rate limiting step. If this was the case, then due to the nucleophilic character of the radical the reverse rate order would be expected

(Herk *et al.*, 1961). The abstraction of a hydrogen atom from the monomer molecule by the initiator, therefore, appears to be the more important reaction. For methyl methycrylate, for example, this reaction could be written as:



$$CH_2 = \underset{CH_3}{\underset{|}{C}} - \underset{O}{\underset{\|}{C}} - OCH_3 + \overset{--}{SO_4^{\cdot}} \longrightarrow CH_2 = \underset{.CH_2}{\underset{|}{C}} - \underset{O}{\underset{\|}{C}} - OCH_3 + \overset{-}{HSO_4}$$

The experimental observation that the rate is proportional to the square root of the initiator concentration (at low initiator concentrations) is also consistent with the equation for rate given earlier. At higher initiator concentrations the order was greater than half. One way of explaining this observation is by assuming that initiator radicals are also generated, in addition, by bimolecular collisions between the initiator molecules.

The increase in rate with the concentration of rubber in latex as well as the probable dependence of rate on the surface area of rubber particles, shows that one of the propagation steps is the reaction of monomer with the rubber. If the propagation step takes place only by $M\cdot_n + M \longrightarrow M\cdot_{n+1}$, the rate of disappearance of monomer would not be expected to depend on the rubber concentration or its surface area.

The effect of solvent on rate is most probably associated with the different stabilities of the initiator radical in different solvents. The lower rates of polymerisation in protic solvents compared to dipolar aprotic solvents could be explained on the basis of solvation of the initiator radical $SO_{\bar{4}}^{\;-}$ by hydrogen bonding. The initiator radical would then be expected to be more stable and thus less reactive.

CONCLUSION

A general survey of the factors affecting the rate of polymerisaton of vinyl monomers in field latex has been carried out. From the results it has been possible to draw certain conclusions regarding the mechanism of the reaction. For example, the influence of monomer concentration and initiator concentration (at low concentrations) on the rate is consistent, at low conversions, with a simple free radical mechanism. It also appears from the results that free radicals are formed on the monomer by hydrogen abstraction rather than by addition, that the propagation step involves, at least partially, the addition of monomer to rubber, that solvation effects are important. The kinetics become increasingly complex as the reaction proceeds. Perhaps diffusion and viscosity problems then become more important.

This work is not yet complete. Two aspects that we hope to investigate further are the reason for the rapid fall off in rate with conversion, and mechanism of initiator action.

A new line of approach to graft polymersation is to start with a rubber molecule with "built in" initiator groups. Recent work of one of the authors at the NRPRA showed that hydroperoxide group could be introduced, without molecular weight degradation, into the rubber molecule. By this method it should be possible to control closely the structure of the grafted products, and thus 'tailor make' molecules to suit particular applications.

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