A T H E S I S

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"STUDIES IN RADIATION CHEMISTRY"

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A B S T R A C T

A comprehensive review is given of the mechanisms of radiation-induced reactions. (Chapters 1 - 3). The solid state polymerization, induced by γ-rays, of methacrylamide (Chapter 4) and N-arylmethacrylamides (Chapter 5) is described and the kinetics involved are discussed. An attempt has been made to correlate monomer structure and reactivity in these reactions. Results of the irradiation of several substituted styrenes in the solid and liquid state are given (Chapter 6) and discussed in terms of polymerization mechanisms.

Appendix I contains a list of infrared absorption bands of N-arylmethylacrylamides (monomers and polymers). An attempt is made to identify the bands of specific groupings by comparison with literature data. The infrared and ultraviolet absorption bands of substituted styrenes are presented in Tables.

Dosimetry in radiation fields of ^{60}Co-sources is described in Appendix II.

A C K N O W L E D G E M E N T S

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NOTE

In this thesis, numbers of formulae etc. are indicated by Roman numerals; Arabic numerals in parenthesis refer to equations, and combinations of Roman and Arabic numerals refer to the page number in the author's experimental notebooks. Arabic numerals superscripts in the main text refer to the list of references given on p. 111 ff; those in Appendix I and Appendix II refer to the references at the end of these appendices.

All melting points have been determined in capillaries and are "uncorrected".

1. The Absorption of High Energy Radiation

1.1. Photochemistry

When visible and near ultraviolet radiation interact with matter, each photon is totally absorbed in a single act by a single molecule of the absorbing medium. The energy of the photon may be calculated from

[1] energy in eV = 12395/λ, where λ is given in $\mathring{A}$

Most molecules cannot be ionized by photons of these wavelengths, as it requires a minimum of 9 - 15 eV to ionize away the most easily removable electrons. Provided the irradiated molecule has an absorption band in the appropriate region, these photon energies are sufficiently high to raise the bonding electrons to higher orbitals, and in this excited state the molecules may dissociate, rearrange, or return to the ground state without dissociation. The radiation energy will appear in dissociation followed by chemical reaction, or in the form of heat; a small part may in some cases appear as fluorescence. This is the basic mechanism of photochemical reaction.

1.2. Radiation Chemistry

Radiation chemistry deals with the chemical

effects of high energy radiations, such as X-rays, γ-rays, α-particles, β-particles and charged particles raised to high energy by accelerating machines. These particles lose their energy in a large number of collisions.

In the case of ^{60}Co-γ-rays, formed in the radioactive decay of ^{60}Co

$$^{60}Co \longrightarrow {}^{60}Ni + \beta^- + \gamma \quad (\beta^- \text{ absorbed in the mantle of the irradiation source})$$

photons of 1.16 MeV and 1.33 MeV are emitted. As a result of photon-molecule interactions, high energy electrons are ejected (Compton-effect*) and give rise to a whole sequence of further ionisations. The higher the energy of the photon, the further apart are the sites of ionisation in the track of a particular photon.

For very roughly each 32 eV of energy expended (by both primary radiation and secondary electrons), one ion pair is produced. Again very roughly, only 15 eV is required to ionize a molecule.[1] Approximately 17 eV of the 32 eV expended is left over for production

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* For radiations of these photon energies, the photo effect and pair formation are normally taken as negligible.

of electronically excited molecules through optically allowed transitions, mainly to the lowest allowed excited state. Such processes correspond exactly to those of the photochemical primary act. On the other hand, slow secondary electrons - of energy 20-100 eV - may give rise to excited states differing in multiplicity from the ground state by optically forbidden transition.

Evidently, the single molecule primarily affected by high energy radiation makes an imperceptible contribution to the overall observed chemical phenomena. For this reason, all high energy radiation, whether particular or electromagnetic, produces very similar chemical effects. The basic mechanism of reactions initiated by high energy radiation ($\lambda \ll 200$ A) is thus quite different from that of photochemical reactions.

1.3. Secondary reactions of ions and excited molecules

The situation arising from the passage of high energy radiation through matter is very complicated in different respects. In our further discussion, we shall deal only with effects of γ-irradiation.

The ion which is produced when a photon or an electron ionizes a molecule

[2] $M + e^{\ominus *} \longrightarrow M^{\oplus} + 2\, e^{\ominus *}$

[3] $M \longrightarrow M^{\oplus} + e^{\ominus *}$

is not the same as the carbonium ion produced by heterolytic cleavage

[4] $RX \longrightarrow R^{\oplus} + X^{\ominus}$

The ion $R^{\oplus}$ has an even number of electrons, whereas $M^{\oplus}$ has an odd number and hence is actually a free radical ion, highly reactive both because of its charge and because of its odd electron.

Immediately after the molecule-radiation interaction, neither the ions formed nor the excited molecules are in an energetically stable form. All species arising from the interaction are carrying different amounts of kinetic and/or vibrational energy. The course of further reactions is determined by these relative energies, by the relative height of excitation levels, ionisation potentials and bond energies. Energy- and ionisation-transfer steps are all influenced by phase effects. Further, the ion- and radical-distribution is inhomogeneous, as ions and radicals lie (especially in solids) in discrete tracks which do not overlap, at least up to high dose rates. Table 1 shows a few of the possible reactions.

Table 1

(a)	$A - B \longrightarrow A - B^{\oplus} + e^{\ominus}$	ionisation
(b)	$A - B \longrightarrow A - B^{*}$	formation of excited molecules
(c)	$A - B^{\oplus} + e^{\ominus *} \longrightarrow A - B^{*}$	
(d)	$A - B^{\oplus} \longrightarrow A^{\oplus} + B$	ion-dissociation
(e)	$A - B^{\oplus} \longrightarrow A + B^{\oplus}$	
(f)	$A - B^{*} \longrightarrow A^{\cdot *} + B^{\cdot}$ ($A^{\cdot} + B^{\cdot *}$ or $A^{\cdot *} + B^{\cdot}$)	dissociation of excited molecules
(g)	$A - B^{\oplus} + e^{\ominus *} \longrightarrow A^{\cdot} + B^{\cdot *}$	
(h)	$A - B^{*} + C \longrightarrow A - B + C^{*}$	energy transfer
(i)	$A - B + e^{\ominus} \longrightarrow A - B^{\ominus}$	electron capture

1.4. Radiation Sensitivity and Protection

It would seem, that in a complex organic molecule all bonds are equally liable to bond breakage under the influence of high energy radiation. This, however, does not occur.

The introduction of an aromatic substituent into an aliphatic hydrocarbon, or the presence of a small concentration of an aromatic compound in a hydrocarbon,

gives rise to a large reduction in the G-value[2,3] (G= number of molecules changed/100 eV). The aromatic ring is evidently so much more stable than alicyclic or aliphatic structures, that it can absorb not only the energy it receives directly, but also a large fraction of the energy received by the saturated component. This effect has been called "sponge"-protection.[4] Experiments on this line have been carried out by several groups of investigators with mixtures of cyclohexane and benzene, and cyclohexane and iodine under different conditions.[5] Energy transfer effects in solutions of polyisobutylene in the presence of unsaturated hydrocarbons, e.g. di-iso-butylene, have been described by Henglein and Schneider.[6]

Available evidence does not yet permit a decision between two proposed mechanisms for energy transfer: emission of a virtual photon or charge transfer. Virtual photon transfer to the stable additive may be a one-step long range transfer or - in condensed phases - a series of transfers from solvent molecule to solvent molecule, until the excitation energy is localised and trapped in the additive.[7] The theory of transfer of excitation energy is not new; it is essentially a coupling between two resonant oscillators.

Since aromatic groups can exert protective effects by intermolecular energy transfer, it is to be expected that they will have at least equally powerful intramolecular effects and should very effectively protect susceptible groups located within the same molecule. This has been clearly demonstrated by Alexander and Charlesby for copolymers of iso-butylene and styrene[8,9] and for substituted dodecanes.[9] Similar results, showing an increased radiation resistance of aromatic systems, have been obtained by Magat[10] and Pahl[11] in experiments concerned with effects of electron impact on organic molecules.

Isolated carbon-carbon double bonds seem in some cases to have the effect of energy traps. Charlesby[12] reported that the dose required to produce a gel network in linear hydrocarbons containing a double bond at the chain end, was about 60 per cent of the dose required for the homologous saturated hydrocarbons. Vinylidene- and vinyl-unsaturation in polyethylene decreases under irradiation much more rapidly than would be expected on a random basis; Dole and Keeling[13-15] found a G-value of ten for the disappearance of vinyl groups in polyethylene.

2. Effects of High Energy Radiation on Organic Liquids and Solids

2.1. Introductory remarks

Whereas in the gas phase excited molecules or ions may exist long enough to undergo dissociation or other reactions, this is less likely to happen in liquids and solids, where we find a much higher collision rate and a rapid recombination of the ejected electrons with their parent ions. It follows, that in pure organic liquids and solids, nearly all chemical reactions start from excited molecules which subsequently lose their energy by internal conversions, collisions or dissociation into free radicals.

Recently, however, some evidence has been found which suggests the contribution of ionic species in low temperature polymerizations (see chapter 3.3).

2.2. Irradiation of saturated aliphatic solids of low molecular weight

Relatively little work has been done in this field, and the few results available do not yet allow any definite conclusions.

Lemmon and co-workers[16] found on irradiation of choline chloride with different types of radiation (^{60}Co-γ, ^{14}C-α, 2-4 MeV electron beam), a chain reaction yielding exclusively acetaldehyde and trimethylamine. Small changes in the molecule reduce the G-value to a considerable extent (table 2).

Table 2

Irradiation of choline derivatives with ^{60}Co-γ-rays

G-values for 10% decomposition (room temperature)

$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ Cl^{\ominus}$	354
$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ Br^{\ominus}$	92
$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ I^{\ominus}$	2.5
$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ NO_3^{\ominus}$	4.9
$[(CH_3)_3NCH_2CH_2OH]_2^{\oplus}\ SO_4^{\ominus}$	29
$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ CN^{\ominus}$	16
$[(CH_3)_2(C_2H_5)NCH_2CH_2OH]^{\oplus}\ Cl^{\ominus}$	26
$[(CH_3)_3NCH_2CH_2OH]^{\oplus}\ Cl^{\ominus}$ in H_2O	2 - 4.4

Irradiation at -170°C gave practically no decomposition, but on warming up, the usual products were

gradually formed. Electron spin resonance measurements (ESR), showed the presence of one free radical formed per 10^4 eV, which decayed at room temperature with a half life of 4 hrs., in good agreement with the analytical results obtained for the decomposition rate of choline chloride. The presence of iodine vapour had no influence on the G-values. A dose rate effect was found but not quantitatively estimated; low dose rates gave, in experiments with equal dose, a higher decomposition rate.

Equally interesting, are the experiments on temperature effects. Serlin[17] showed that for γ-rays the G-value for disappearance of choline chloride was higher at 50°C than at 20°C, but at 150° the solid choline chloride was much more radiation-resistant than at room temperature. Subsequently, Collin[18] carried out X-ray diffraction studies on both powder and single crystals, as well as an investigation of cooling curves. He found, by all methods, a phase transition in the range between 73°C and 78°C, and showed that the low temperature regular orthorhombic unit cell is transformed at higher temperatures into a disordered face centred cubic unit cell. Collin concluded that this increased stability of the disordered high temperature

form is evidence for the highly stereospecific decomposition of choline chloride, keeping in mind that its aqueous solution shows no exceptional radiation sensitivity.

Willard and co-workers[19] reported work on the effects of structure and phase on the radiolysis of alkyl iodides.

Table 3

G (I_2) for ethyl iodide; dose 2.26 x 10^{19} ev/g

	20°	-78°	-120°	-190°(cryst.)	-190°(glass)
G	4.25	4.38	2.05	0.95	3.05

On slow cooling, ethyl iodide solidifies in crystalline form; quick cooling gives a glassy solid.

These results seem to be contradictory to the ones obtained from choline chloride. In the case of ethyl iodide, the disordered, glassy state seems to be more favourable for the formation of iodine than the crystalline state. Willard suggested that the difference may be due merely to a molecular arrangement within the crystal which renders iodine production from ethyl iodide difficult.

2.3. Irradiation of high polymers

The irradiation of high polymers is of considerable industrial interest, as relatively low doses - causing only one or two changes per molecule - change the mechanical properties of the polymer to a considerable extent. Recently, two monographs on this wide subject have been published.[20,21]

2.4. Trapped radicals

Energetic ultraviolet light, X- and γ-rays have been shown to break bonds resulting in the formation of free radicals. In the solid or frozen state, these radicals become frozen at some distance from each other, as the high energy radiation imparts the radical ends of the fragments with sufficient kinetic energy to move away with some speed. If the solid is too rigid, the radicals stay in the immediate neighbourhood of each other and recombine easily.

Trapped radicals have been produced in many inorganic and organic crystals, in different polymers and in glasses of hydrocarbons.[22,23] Their presence may be detected by chemical methods, such as graft co-polymerization, or reaction with stable organic radicals e.g. diphenylpicrylhydrazyl (DPPH), or by physical measure-

ments such as magnetic susceptibility or electron spin resonance. In some cases it has been possible to establish the actual structure of radicals by ESR-methods, but superimposition of spectra of different radical species - some of them only transient - often makes identification difficult.[24]

The steady-state concentration in a free radical polymerization is in the region of 10^{-8}M and is just about the maximum detectable by present day ESR-spectrometers. By irradiating solids with γ-rays or high energy electron beams, much higher concentrations - up to 10^{-2}M - can be obtained. After irradiating solid acrylamide with γ-rays, Ballantine[25] found a steady state concentration of 10^{-4}M. The same author suggested the possibility of storing chemical energy in this way, as these radicals have, under suitable conditions, half-lives of several weeks or months.

If the irradiations are carried out in the presence of oxygen (air), or if oxygen is admitted to the sample after irradiation, peroxyl radicals are formed. These radicals are again rather stable entities in solids, but they may react with neighbouring radicals or by hydrogen abstraction from a neighbouring methyl(ene)

group resulting in the formation of a new radical.

3. Radiation-Induced Polymerizations

3.1. Introduction

Radiation-induced polymerizations have been investigated under different conditions: in the gas phase, liquid phase and solid phase; in solution, emulsion and dispersion. Recently, summarizing reviews have been given by Chapiro and Magat[26] and by Charlesby.[27]

The polymerization of monomers involves at least three separate steps, i.e. chain initiation, chain propagation and chain termination. Vinyl polymerization can be initiated either by free radicals, or ions or both, varying with the structure of the monomer and the reaction conditions. The kinetics of free radical polymerizations are fairly well known; ionic polymerizations are much less well understood. Different ionic reaction systems seem to react in very individual ways, especially concerning the importance of co-catalysts in these reactions.

3.2. Free radical polymerization

Most of the radiation-induced polymerization

reactions studied up to now, have been found to proceed by free radical mechanisms.[26,27] The available evidence for this mechanism has been summarized by Swallow[27]:

1. Benzoquinone, DPPH and similar inhibitors of free radical polymerization are effective in radiation-induced polymerization under widely different conditions.

2. The polymerizations are sensitive to the presence of oxygen which reacts with the free radicals formed to give peroxides.

3. In aqueous solution, polymerization of acrylonitrile can be initiated by γ-rays, although under these conditions it cannot be initiated by ions.[28]

4. The rate of polymerization is often proportional to the square root of the radiation intensity. This dependence on the initial radical concentration is typical of many free radical polymerizations, where the termination step occurs by combination or disproportionation of two growing chains.

5. Radiation-induced co-polymerization experiments[29,30] have been found to give products of identical polymer composition with those from free radical initiated co-polymerizations.

6. The activation energies of photo- and γ-ray polymerizations of several monomers have practically identical values.

7. The polymerization rate increases linearly with the temperature.

8. The polymerization rate is independent of the dielectric constant of the solvent.

Although very little is known about the nature of the radical chain initiating species, practically all radiation-induced polymerizations follow the given outlines.

For low conversions, the propagation and termination steps follow the kinetics of free radical-initiated vinyl polymerizations, as described by different workers.[31] If the dose rate is high and the monomer concentration low, then the concentration of the initiating radicals increases and the termination begins to include interactions between initiating

radicals, and between them and growing chains. This leads to polymers of relatively low molecular weight. Consequently, the rate of polymerization becomes proportional to (dose rate)^{x}, where $x \longrightarrow 0$.

In precipitating media, $x \longrightarrow 1$, as the growing chain ends are no longer freely accessible to monomer and the rate of termination is decreasing. This acceleration phenomenon is well known from free radical--initiated vinyl polymerizations in precipitating or highly viscous media.[32]

In the case of photolytic or γ-ray initiation, this delayed termination has the further consequence that the polymerization continues after completion of the irradiation, for several days or longer. These post-effects are not restricted to cases involving precipitation of polymer from solution,[33] but have been found also in completely homogeneous systems, such as nucleic acid in water,[34] and poly(acrylamide) in water.[35,36]

3.3. Ionic polymerization

3.3.1. General remarks

Samuel and Magee[37] calculated that an electron

ejected from a water molecule returns to its parent ion after about 10^3 collisions. Experimental evidence obtained up to now, confirms that in liquids at about room temperature, the parent ion recombines with the ejected electron within 10^{-13} - 10^{-14} sec; i.e., before the ion is able to undergo an addition reaction. Under these conditions, all polymerization reactions will therefore be of the free radical type as already described.

In the model of Samuel and Magee, the electron will be recaptured by its parent ion, if the distance between ion and electron at the moment the latter becomes thermalized (kinetic energy = $kT \approx 0.025$ eV) is smaller than a critical distance R_c, defined as

$$kT = \frac{e^2}{\varepsilon . R_c} \qquad [5]$$

where e = charge of electron

ε = dielectric constant of the surrounding for vibrations $\nu \geq \Delta\tau^{-1}$

$\Delta\tau$ = ion life time $\approx$ free electron life time

If $R > R_c$, the coulomb attraction is too weak to bring about ion-electron recombination. The electron will be completely free and react with any positive ion in its surroundings.

3.3.2 Influence of phase on $\Delta\tau$

It has long been suspected, that the rate of ion-electron combination will be different in the liquid phase and in the gas or solid phase. In the gas phase, the collision rate will be lower than in the liquid phase, at least around room temperature and/or at pressures below atmospheric. This decrease in collision rate increases the life time of free ions, and one observes reactions following an ionic mechanism.[38]

Lautout[39] has shown, that for the case of ionic crystals and glasses, the electron "traps" are deep enough to stabilize the positive ions for rather long periods, even within the critical distance R_c. For non-ionic crystals, much less is known. One might think of the possibility of long-living positive ions formed by the mechanism discussed, or of the formation of equally stable carbanions by electron capture.

3.3.3. Influence of temperature and solvent on $\Delta\tau$

Platzmann and Froehlich[40] suggested that the life time of "subexcitation electrons", i.e. electrons with energies between 0.025 eV and 0.2 eV, would be a function of the temperature. They calculated that the rate of energy dissipation for aliphatic chlorides

would be 10^{11} eV/sec at 300°K, but only 10^{8} eV/sec at 100° K. It follows, that the life time of a free electron is 10^{3} times higher at 100°K than at 300°K.

If the electrons move on the general lines of Brownian movement, their relative pathlength will be equal to the relative thermalization time t. The distance R between the parent ion and the thermalized electron is given by the theory of Brownian movement:

/6/ $$R \alpha t^{0.5}$$; it follows

/7/ $$R_{100^\circ K} \approx 30\, R_{300^\circ K}$$

From eq. /5/ we get

/8/ $$R_c(100^\circ K) = 3R_c(300^\circ K)$$

Following Platzmann[41], the value of $R_{300^\circ K}$ is of the order of 50 Å, whereas $R_{c(300^\circ K)}$ for a dielectric constant of 4 is 150 Å.[37] It follows, from /7/ and /8/ that at low temperatures $R > R_c$; i.e., the electron will not return to its parent ion, but react with any positive ion in the surroundings.

Magat[42] has tentatively calculated the average life time of positive ions for an irradiation intensity of 1000 r/min., yielding under steady state conditions

3 ion pairs per 100 eV, and therefore producing an ion concentration (of either sign) of $n = 9.10^{-10}$ mol/l. The rate of recombination of a positive ion and a free electron under the conditions mentioned would be

$$-\frac{dn}{dt} = \alpha . n^2 \qquad [9]$$

Taking the recombination coefficient for H^+ and OH^- ions in water[43-45] (5.10^{10} l/mol.sec), the life time $\Delta\tau$ of a positive ion was calculated to be of the order 10^{-2} sec.

As the activation energy for a propagation step in a cationic polymerization is very low - and the time required very short - one arrives at conditions where the life time of the positive ion seems long enough for a cationic chain reaction to occur. As $\Delta\tau \alpha I^{-\frac{1}{2}}$, the chain length would not be determined by the neutralization step, even at intensities up to 10^7 r/sec. One would expect the polymerization rate to be proportional to the radiation intensity I up to high dose rates. Experimental evidence for this theory has been forwarded by different workers and will be discussed in the next chapter, and in connection with our results from irradiation experiments on substituted styrenes.

Similar conditions would be expected for the electron capture by molecules with strong electron

affinities, such as O_2, benzoquinone, halogen- and cyano-compounds. The polymerization tendency is further increased in a surrounding of high dielectric polarization, (eq. [5]). Experiments made recently on these lines seem to prove this assumption.

3.4. Polymerization in the solid state initiated by γ-rays

3.4.1 Polymerization of high-melting vinylic monomers

Since 1954 several papers have been published by workers in Germany and in the United States. The German group[46-48] dealt mainly with changes in single crystals of acrylamide under the influence of γ-rays, whereas the American group[49,50] reported a first list of compounds which they had been able to polymerize in the solid state (Table 4). They also undertook a first study of the kinetics of the reaction, without arriving at any final conclusions about the influence of dose, dose rate and temperature.

At this point, we commenced research on the solid state polymerization of methacrylamide and its derivatives. Preliminary experiments showed that the polymerization of methacrylamide went on after the end of

Table 4

Compound	Dose rate rep/hr. 10^{-5}	Temperature °C	Initial rate % conversion/ hr.
Acrylamide	1.9	30	12.8
Methacrylamide	3.1	30	0.7
Acrylic acid	3.1	- 18	400
Methacrylic acid	1.9	- 18	400
Ca - acrylate	1.9	35	18.1
K - "	1.9	35	56.8
Ba - "	1.9	35	75.1
Vinylstearate	1.9	26	20.0
Vinylcarbazole	2.2	30	1.1

No reaction with: maleic anhydride, allylamine hydrochloride, allylamine picrate and stilbene.

the irradiation; a fact which was not yet known from the literature for this type of reaction. We established the course of this post-irradiation effect in air for periods up to 660 hrs., and started work on the kinetics of the "in-source" reaction over a wide range of dose and dose rate.

During the course of this second part of our research, the American group published more detailed

results about their studies on acrylamide, using crystal-optical and physico-chemical methods for establishing the kinetics of the reaction.[53a-d] Their findings included the discovery of a post-irradiation effect in acrylamide, a factor which invalidated most of their previous experimental results.

Our experiments with methacrylamide and some of its derivatives have therefore been carried out independently of the most recently published work on acrylamide. In the discussion of our results, however, we shall try to make comparisons between these results and shall use as far as possible, the same symbols and definitions.

3.4.2 Polymerization near the melting point[51,52]

a) Hexamethylcyclotrisiloxane (m.p. 64°)

This non-vinylic compound could not be polymerized using free radical initiators, such as benzoyl peroxide or $\alpha\alpha'$ azodi-isobutyronitrile. The polymerization rate, under the influence of high energy electrons, increased from 1%/Mrad at 10°C to 10%/Mrad at 60°C, dropping to practically zero above the melting point. The apparent activation

energy for polymerization in the solid state was found to be 10 kcal./mol, and, for equal dose, the reaction proceeded faster at lower dose rates. In a more recent study, Burlant and Taylor[52] found an even higher polymerization rate (35%/0.25 Mrad) and no dose rate dependence.

b) Vinylstearate (m.p. 34°)

The polymerizability of this compound in vacuo in the solid state has been briefly described by Restaino et al.[50] Burlant and Adicoff[54] irradiated the same compound in the presence of air; they found air to be an inhibitor, at least for low dose rates. For high dose rates, the reaction rate was found to be linear with the field intensity, and the molecular weight to be independent of the dose rate for a given total dose. The temperature dependency of the polymerization rate of vinylstearate was found to be somewhat different from that of hexamethylcyclotrisiloxane. In the crystalline state, well below the melting point, the reaction rate was lower and the molecular weight higher than in the liquid

phase, the second finding being contrary to the results of Restaino. On approaching the melting point, the polymerization rate increased rapidly. At a slightly higher temperature, reaction rate and molecular weight dropped considerably, the former slowly increasing, the latter decreasing at higher temperatures. Addition of 0.1% α,α' diphenylpicrylhydrazyl lowered the polymerization rate until the inhibitor was exhausted, whereupon the rate increased sharply and approached that of the pure monomer.

c) Styrene[55]

Styrene showed practically no reaction on irradiation at -78^{o}. On warming up, an "out-source" effect, several times higher than the "in-source" effect, was found. The reaction rate increased during thawing up of the sample, but dropped to zero in the liquid phase. Benzoquinone had, rather surprisingly, a rate increasing effect.

d) Acrylonitrile

Sobue and Tabata[56] irradiated acrylonitrile over a wide range of temperatures, finding a first

maximum in the reaction-rate at -130°C, in the crystalline solid state, no reaction at -78°C in the solid glassy state and a free radical polymerization with a positive temperature coefficient in the liquid state.

e) Ethenesulphonamide

Wiley and Gensheimer[57] gave a preliminary report of their work on the irradiation of ethenesulphonamide in the solid state, near the melting point. The reaction rate found was very high, but the results were not reproducible.

f) Isobutene

The radiation-induced polymerization of isobutene in the liquid state at low temperatures has been very thoroughly investigated; it is still the cnly one where an ionic mechanism has been convincingly proved to occur. The reaction has been described in detail by Pinner, Worall and Charlesby[58] and further discussed by Dainton and Collinson.[59] It has been found that certain solid additives, such as ZnO, increase the polymerization rate considerably.

4. Polymerization of methacrylamide in the solid state, induced by γ-rays

4.1. Introduction

As has been shown by different workers,[*] a variety of monomers can be polymerized in the solid state by exposure to gamma radiation. We have investigated the solid state polymerization over a wide range of dose and dose rate, in the presence and in the absence of oxygen, and will present separate conversion versus time curves for polymerization during and after irradiation (in-source and out-of-source polymerization, respectively). The kinetics of these reactions will be discussed.

4.2. Experimental

Methacrylamide was dried on a high vacuum line. After sublimation, pure white material, m.p. 108-109°, was obtained.

Preparation of irradiation samples. Weighed samples of methacrylamide were evacuated in glass tubes (diameter 1.2 cm. or 0.6 cm.) under high vacuum, and the tubes sealed under vacuum, or together with dry air.

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[*] see chapter 3.4.

Irradiation

80 C - Source (nominal): All samples were irradiated at room temperature at a constant distance (4 cm.) from the ^{60}Co - source. The measurement of the field intensity is described in Appendix II.

1000 C - Source (nominal): The samples were irradiated at room temperature (unless stated otherwise) at various distances from the ^{60}Co - source. We are indebted to Mr. M. Street of the Nuclear Technology Department of Imperial College for the calibration curve (Appendix II).

In both cases, the rate of energy input was corrected to current dates in accordance with the known decay rate of the cobalt; the small difference between the electron densities of water and of organic compounds was neglected.

Determination of conversion

The tubes belonging to in-source experiments were opened immediately after irradiation; the samples used for post-irradiation experiments were stored at room temperature or opened and kept in a desiccator at room temperature. After opening, the monomer conversion was determined by one (or both) of the following methods.

4.2.1 Gravimetric determination of monomer conversion

A weighed amount of irradiated monomer was thrown with stirring into a large volume of methanol or chloroform which are good solvents for the monomer and in which the polymer is insoluble. The polymer was crushed and separated by centrifuging. It was washed with methanol, centrifuged, transferred to a weighed glass tube with a ground glass joint and dried overnight on a high vacuum line ($p < 10^{-3}$ mm.) at room temperature. In some cases, the polymer was dissolved in a small volume of water, freeze-dried and finally dried at 60^{o} under high vacuum. The exact sample weight was determined in all experiments by re-weighing the empty irradiation tube and subtracting this value from the original weight of tube plus sample.

4.2.2 Titrimetric determination of unchanged monomer.[60]

Reagent: A mixture of potassium bromide (35.8 g.), and bromine (17.2 g.) was dissolved in water and made up to one litre. This reagent (0.2 N) was standardized daily by drawing reagent (15 ml.), potassium iodide solution (15 ml. of 20 %) and water (about 100 ml.), through a piece of rubber tubing into an evacuated bromination flask

with tap. After shaking for 10 minutes, the vacuum was released, the stopper removed, and the solution titrated with standard 0.05 N sodium thiosulphate to the starch end point.

Procedure: A weighed amount of methacrylamide was added to crushed ice (ca. 50 g.), in a bromination flask. The reagent (60 - 80 % in excess) was sucked in from a burette, the tap closed, and the flask shaken for 20 minutes in a mechanical shaker. Potassium iodide solution (ca. 15 ml. of 20%) was added from a pipette, the vacuum released and the mixture titrated as given for the blank.
1 ml. 0.05 N S_2O_3 corresponds to 2.1285 mg. of methacrylamide. Some results illustrating the accuracy of this method are given in Table 5. These results suggested that experiments with samples of at least 45 mg. methacrylamide, and using a reagent excess of 60 - 80% were reliable within one percent.

Table 5. Bromination of methacrylamide (II, 9 - 11)

weighed (mg.)	found (mg.)	found %	% reagent in excess
65.0	65.2	100.3	70
41.6	40.44	97.2	100
20.8	20.1	96.6	85
44.2	44.23	100.0	58
22.1	21.62	97.6	77
22.1	21.43	97.0	37
98.9	98.4	99.5	46
72.0	71.76	99.5	72

Typical example of titration results on irradiated polymer

(II, 21, 50)

a) Sample 1 was given a dose of 0.9 Mrad in vacuo and then kept open in a desiccator for one month.

b) Sample 2 was given a dose of 2.8 Mrad in vacuo.

c) Sample 11 was given a dose of 13.9 Mrad in vacuo.

The dose rate in these experiments was 0.041 Mrad/hr. Samples of 50-70 mg. were titrated.

Per cent double bonds found (non irradiated monomer = 100)

a) 90.3; 88.7; 88.2; 89.2; 88.4; mean: 88.96 ($\pm$ 0.99)

b) 83.4; 81.6; 80.8; 82.5; 81.8; mean: 82.0 ($\pm$ 1.2)

c) 88.13 (small crystals); 92.41 (large crystals); 91.43 (mixture)

It can be seen, that in addition to experimental errors, a genuine influence of crystal size on the conversion exists. This seems to be compatible with the kinetic characteristics of a solid state polymerization, as discussed below.

Double bonds in polymers (II, 19)

It was necessary to check the influence which double bonds in polymers have on the titration result. The polymer was isolated by the gravimetric method described, a small sample dissolved in water and titrated following the standard method described. The titration result corresponds to the total bromine reaction with absorbed monomer, double bonds in the polymer and hydroperoxide groups, ("monomer double bonds in polymer").

Table 6 Monomer conversion (corrected)

	a	b	m	n
Irrad. 1	11	89	0.046	88.5
Irrad. 2	18	82	0.042	81.25
---	40	60	0.05	57.4

where: a = monomer conversion found, %
b = monomer unchanged, %
m = fraction of "monomer double bond" in polymer
n = b - a.m. = monomer unchanged, % (corrected)

Table 6 demonstrates that the contribution of "double bonds in the polymer" lies within the limits of experimental error of the monomer determination.

4.2.3 Material balance in combination of the gravimetric and titrimetric method (II, 34)

Some experiments have been carried out to establish the material balance of monomer and polymer. The polymer yield was determined gravimetrically (in chloroform), the unchanged monomer by titration.

Table 7. Material balance of polymer and monomer

Irrad.	% polymer	% monomer	balance (%)
6	10.0	91.0	101.0
	14.5	83.0	97.5
	21.8	75.7	97.5
8	22.5	81.5	94.0
	24.1	77.2	101.3
	27.4	71.5	98.9
	42.7	60.6	103.3
9	25.6	74.0	99.6
	33.2	67.2	100.4
	36.9	62.0	98.9
10	49.3	52.5	101.8
	50.2	47.1	97.3
	52.0	46.4	98.4
	55.1	42.7	97.8

Taking into account the experimental errors of the monomer and polymer determinations, the material balance seems satisfactory.

Unchanged monomer was identified after chromatographic purification on a column (alumina) by its melting point and mixed melting point with pure monomer.

4.3. Experimental results

For the sake of convenience, we follow the example of Baysal et al.[53c] and separate at least initially the in-source reaction from the out-of-source reaction, although the two reactions overlap for long irradiation times.

4.3.1 In-source polymerization

The data on conversion versus time for the in-source polymerization, showing the influence of dose rate and oxygen (air), are given in Figs. 1 - 4.

Discussion

The propagation rate equation used in conventional homogeneous polymer kinetics is

$$[10] \qquad \frac{d\,M}{dt} = k_p [\bar{M}][\bar{R}] \quad ,$$

where k_p is the propagation rate constant, $[\bar{M}]$ the monomer concentration and $[\bar{R}]$ the concentration of growing chains. Usually, a steady state concentration of $[\bar{R}]$ is assumed, and at low conversions the rate of polymerization is constant and decreases at higher conversions as $[\bar{M}]$ decreases.

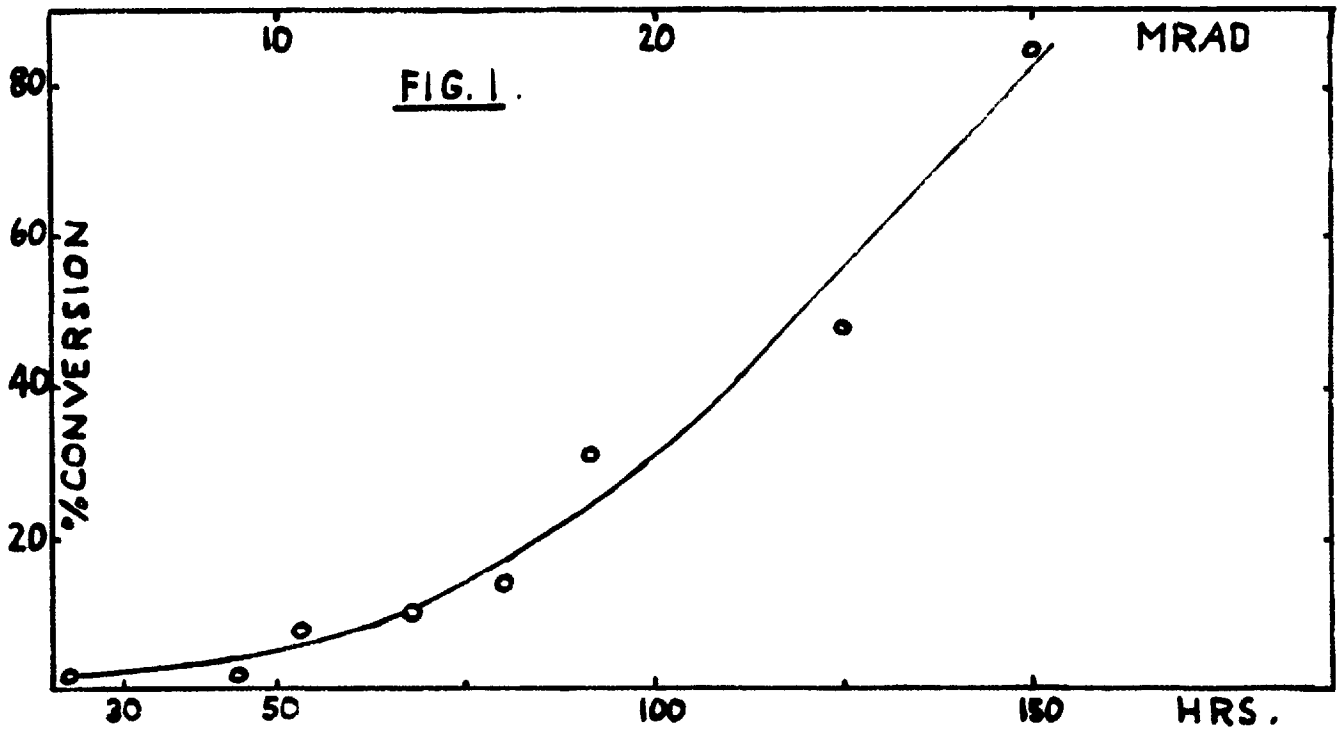
If one considers Figs. 1 and 2, in which are plotted conversion to polymer versus time (dose), it can be seen that the rate is not constant, even at low conversions. The rate actually increases linearly to about 8 - 10 % conversion at which point an acceleration occurs. Such an acceleration effect has been previously reported by Baysal et al.[53c] for acrylamide, where it occurs around 20 % conversion, but at a much lower total dose (1.4 Mrad).

If we assume that k_p is constant, at least at low conversions, the increasing rate can only be explained by an increase in $[\bar{R}]$, thus eliminating any steady state kinetics.

$[\bar{R}]$ may be related to the radiation intensity I by the expression

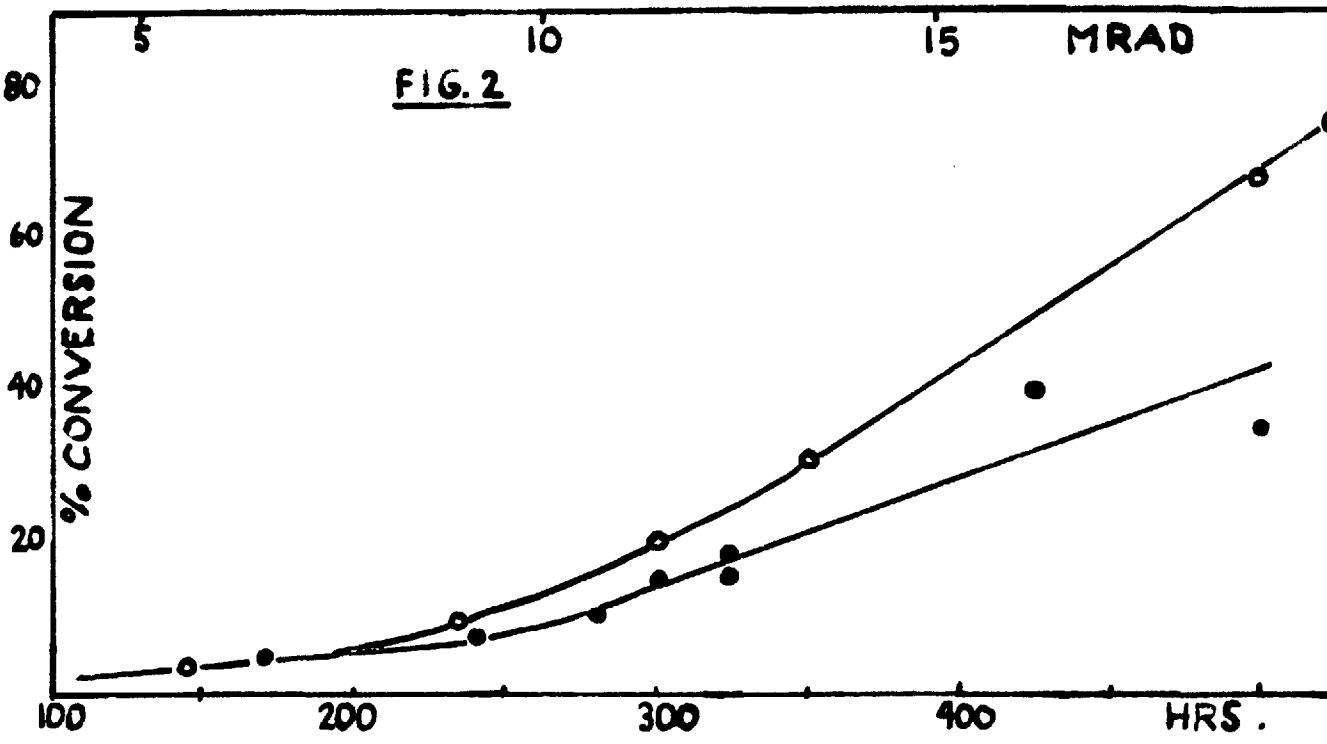
[11] $$R = KI\,t \quad , \text{ where}$$

K is a constant composed of an initiation rate constant



IN-SOURCE POLYMERISATION OF METHACRYLAMIDE

FIG.1. IN VACUO; 0.2 MRAD/HR. o
FIG.2. IN VACUO; DOSE RATE 0.038 MRAD/HR. o
IN AIR ; 0.038 MRAD/HR. ●



k_i and also an efficiency factor f. This assumes that the results of electron spin resonance studies on irradiated acrylamide[53c] are correct and can be applied as well to methacrylamide. Instead of eq. [10] we can now write

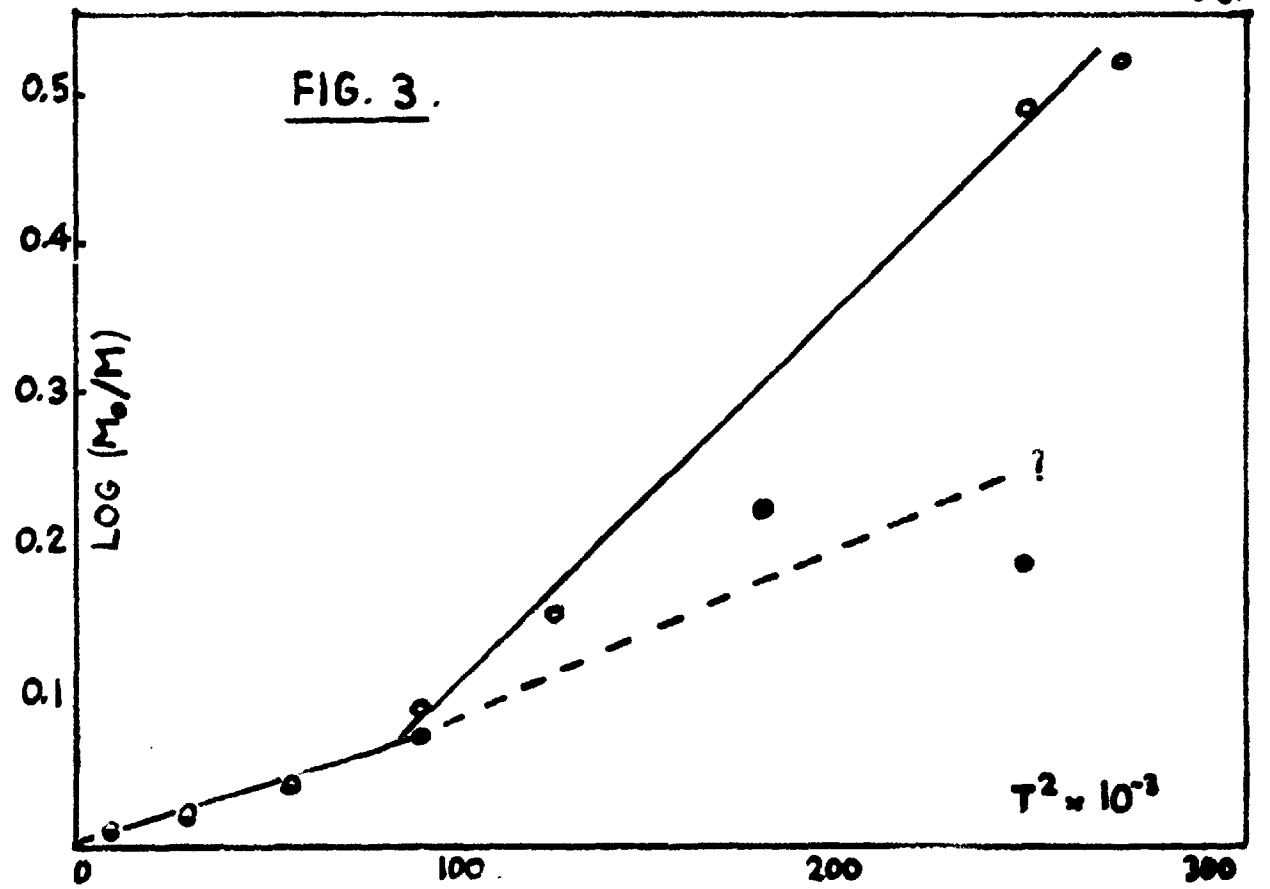
[12] $-dM/dt = k_p k_i f I t [M]$, which in integrated form is

[13] $\log \frac{M_0}{M} = k_p k_i f I t^2 / 4.606$, where

I is constant for any one series of experiments.

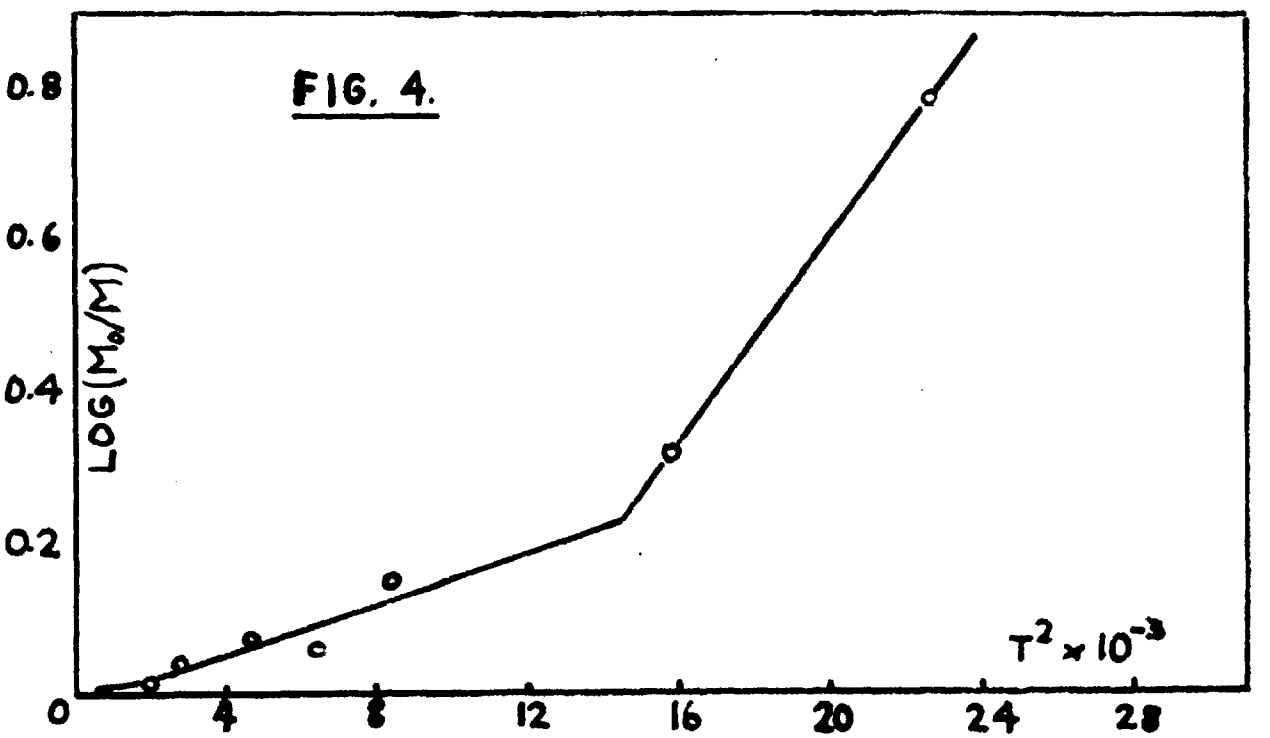
Then a plot of log M_0/M versus t^2 should give a straight line with a slope of $k_p k_i f I / 4.606$. Such plots are given in Figs. 3 and 4 for different intensities. These plots show that the relationship holds for a dose rate of 0.04 Mrad/hr. up to about 15% and for a dose rate of 0.2 Mrad/hr. up to about 25%. A second constant slope seems to occur at higher conversions.

Baysal et al.[53c] attributed a corresponding effect in acrylamide to a sudden increase in the efficiency factor f in eq. [13], suggesting that this might be due to a critical change in the crystals, such as the strain caused by an increase in density which accompanies polymerization. The possibility of a



IN-SOURCE POLYMERISATION OF METHACRYLAMIDE

FIG. 3. IN VACUO; DOSE RATE 0.038 MRAD/HR. o
IN AIR; DOSE RATE 0.038 MRAD/HR. •
FIG. 4. IN VACUO; 0.2 MRAD/HR. o



temperature increase due to polymerization was excluded, after irradiation experiments with thermocouples inserted into the samples showed no temperature increase. In the case of methacrylamide, with its relatively lower polymerization rate, a temperature increase would be even less likely.

These authors believed that a sudden acceleration in rate, such as found in our Figs. 1 and 2 and the break in the yield versus time square curves in Figs. 3 and 4,can be accounted for by a sudden increase in the number of growing chains, and found a simultaneous lowering of the average molecular weight of the polymer formed. Further investigations led them to exclude branching, cross-linking or degradation effects on the polymer.

This theory has certain parallels with results obtained from the irradiation of high density and low density polyethylene. Lawton, Balwit and Powell[61] found that cross-linking occurs mainly in amorphous regions, while trans-vinylene formation occurs as readily in crystalline as in non-crystalline regions at low temperature. Radicals trapped in crystals or glasses do not readily cross-link. When warmed,

they become mobile, form cross-links and disappear. Mobility is an essential requirement for any intermolecular reaction in a solid. It seems reasonable to expect a higher polymerization rate in a crystalline monomer lattice, which gradually becomes disordered due to radiation damage and/or internal strain, due to a change in density. Further evidence pointing in this direction are the influences of small amounts of water (> 1%) and of temperature on the reaction rate in solid acrylamide[50], as well as our results on the solid state polymerization of arylmethacrylamides with different degrees of hydrogen bonding (chapter 5).

Influence of dose rate

Experimental results are given in Figs. 5 and 6. It has to be noted, that for experimental reasons the dose rates are generally very high. It has been shown by different workers[21] for liquid phase polymerizations of styrene, methyl methacrylate, and vinyl acetate, that at field intensities higher than ca. 1000 rad/min., the slope of the curve in a log - log plot decreases. A similar effect has been noted by Restaino et al.[50] in the solid state polymerization of acrylamide for

intensities higher than ca. 6000-30000 rad/min. For methacrylamide, we find a decrease in the slope for intensities higher than 1000 rad/min. (Fig. 5). This decrease is shown even more markedly in a plot of intensity versus conversion/Mrad (Fig. 6). A maximum value is reached at an intensity of 1000 rad/min., and the conversion/Mrad then decreases to level off at a more or less constant low value.

This decrease at higher intensities can be interpreted as arising from the high concentration of radicals, so that a significant proportion of primary radicals react with each other or with growing chains rather than initiating new ones. On theoretical grounds, one would expect that under these conditions, the polymerization rate would be independent of radiation intensity. This result is shown in Fig. 6.

Under these conditions a more detailed analysis of the results is not possible.

4.3.2. Out-of-source polymerization

Introduction

In retrospect, the ideal experimental conditions for studying the post-polymerization of methacrylamide would be irradiation at a temperature sufficiently

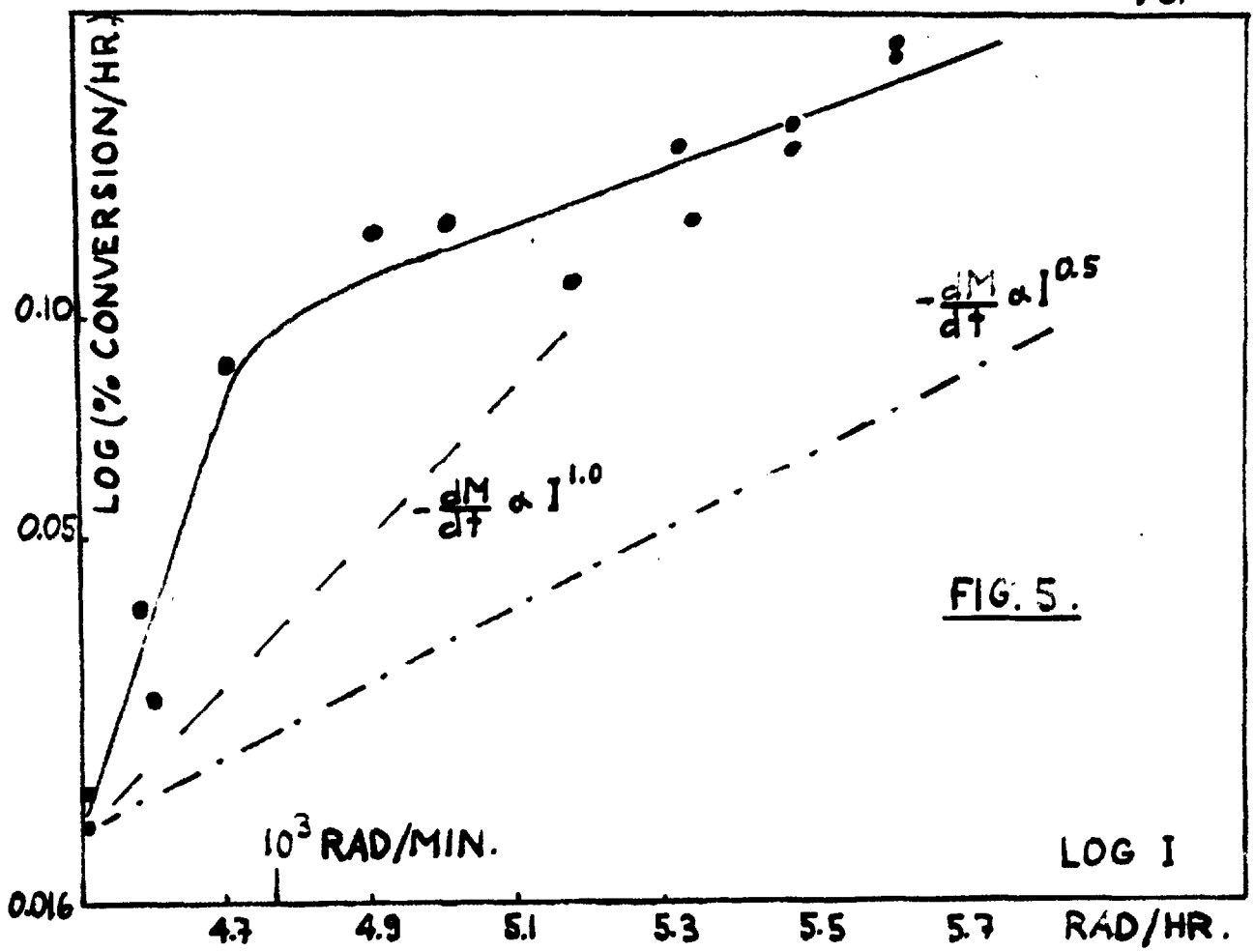


FIG. 5.

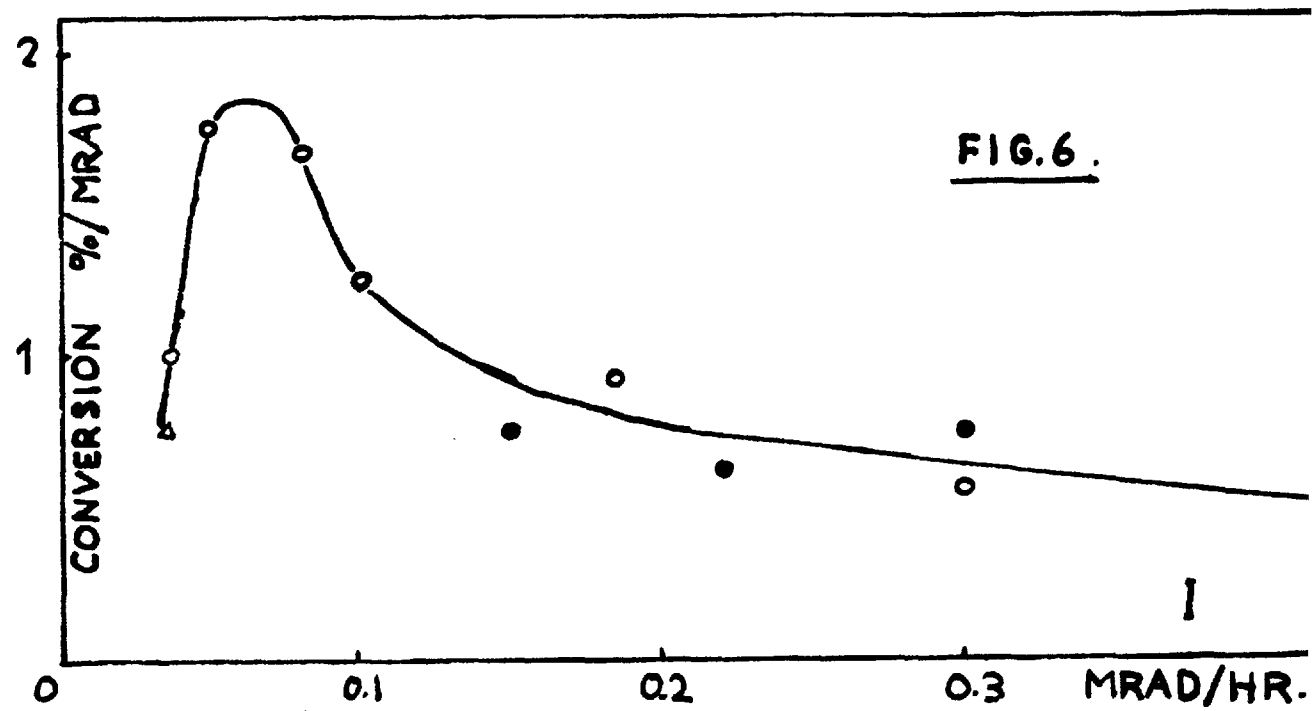


FIG. 6.

FIGS. 5, 6. (IN-SOURCE) POLYMERIZATION RATE VERSUS RADIATION INTENSITY I

low to prevent any in-source polymerization, and then warming to a convenient temperature, so as to allow the monomer to polymerize. The out-of-source polymerization of acrylamide has been studied in this way by Fadner, Morawetz et al.[53a,b] during the course of our work. One important result of their work was the fact, that the ratio of polymer yield to weight average molecular weight changed very little over long periods of time, i.e., they obtained polymers with a narrow molecular weight distribution. These authors also found that the molecular weight of the polymer seemed to be a function, at any given temperature, of the polymerization time only, with little if any dependence on the irradiation dose.

The linear dependence of the polymer yield, for long polymerization times, on the logarithm of the time, was consistent with a chain termination by the interaction of two growing chain-radicals, but this agreement may be accidental, since the ESR spectrum decreased much more slowly than the polymerization rate.

Most of our results on the post-polymerization of methacrylamide have been gained from experiments involving irradiation and storage at room temperature, corresponding to the procedure published recently by Baysal

et al.[53c] Under these circumstances, the starting conditions for studying the post-polymerization were less ideal, as a certain amount of polymer had already been formed, during irradiation. This applies especially to results obtained from experiments using low dose rates (and long irradiation times). A further complication arises from the fact that we stored the irradiated monomer in the presence of air, so that a reaction of radicals with oxygen can take place (see below).

Under these circumstances, we will discuss our results mainly in a qualitative manner rather than quantitatively.

Results

All samples were prepared, irradiated and worked up as described for the in-source reaction.

a) Irradiation at -78°C

The main results are summarized in Table 8.

These results indicate that methacrylamide shows a weak post-effect even at -78°. The post-polymerization proceeds with an average rate of 0.11%/hr. for the first 19 hrs., decreasing to an average of 0.045 %/hr. for the following 168 hrs. A similar

Table 8. Post-polymerization of methacrylamide, irradiated at -78°C (II, 67 - 69)

dose rate 1.0 Mrad/hr.; total dose 24 Mrad

Irrad.	post-irradiation treatment	% conversion
25 a)	worked up immediately	0.05
b)	kept open in desiccator for 19 hrs. (20°)	2.1
27 a)	kept sealed for 19 hrs. at 20°C	3.2
b)	as a), then kept open in desic. for 187 hrs.	5.8
26	kept sealed for 187 hrs. at 20°C	9.7
28	kept sealed for 187 hrs. at -78°C	0.7

rapid decay of the polymerization rate has been found for acrylamide under corresponding conditions.[53a-c] The influence of oxygen on the post-polymerization rate will be discussed at the end of this chapter.

b) Irradiation at room temperature (15 - 20°C) (II, 28-51)

All samples were opened after irradiation and kept in a desiccator. Monomer samples were titrated at intervals. $[\overline{M}_0]$ is in all cases taken as the monomer concentration at the end of the irradiation (= 100%).

Results and discussion

As the rate of polymerization decreases continuously, the possibility of a bimolecular termination step must be investigated.

[14] $-dR/dt = k_t R^2$, leading to a radical decay of the form

[15] $R = R_0/(1 + k_t R_0 t)$, and a polymerization rate

[16] $-dM/dt = k_p [M] [R_0] / (1 + k_t R_0 t)$

The loss of monomer is given by

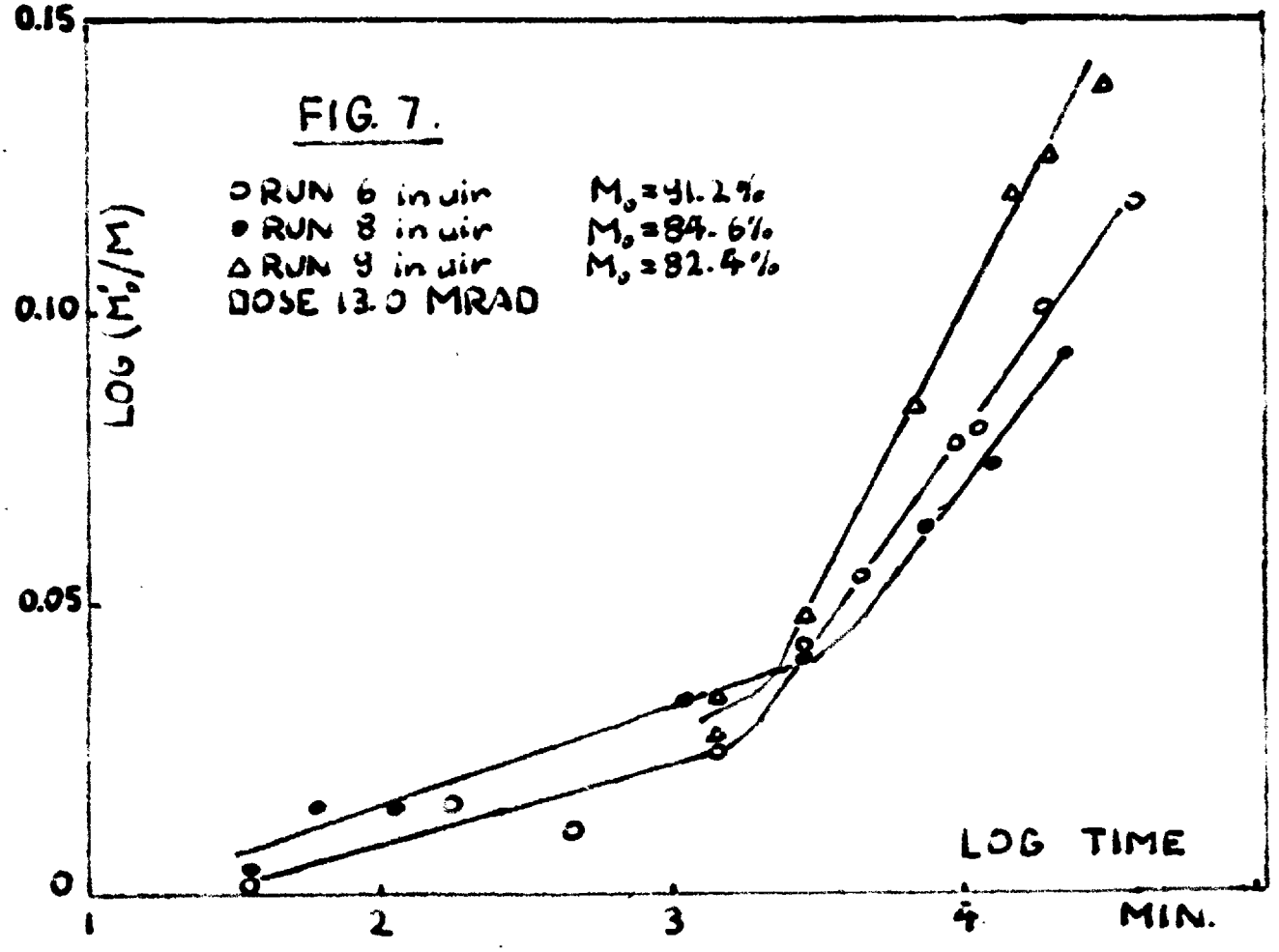
[17a] $\lg M_0/M = k_p/k_t \cdot \lg (1 + k_t R_0 t)$, or

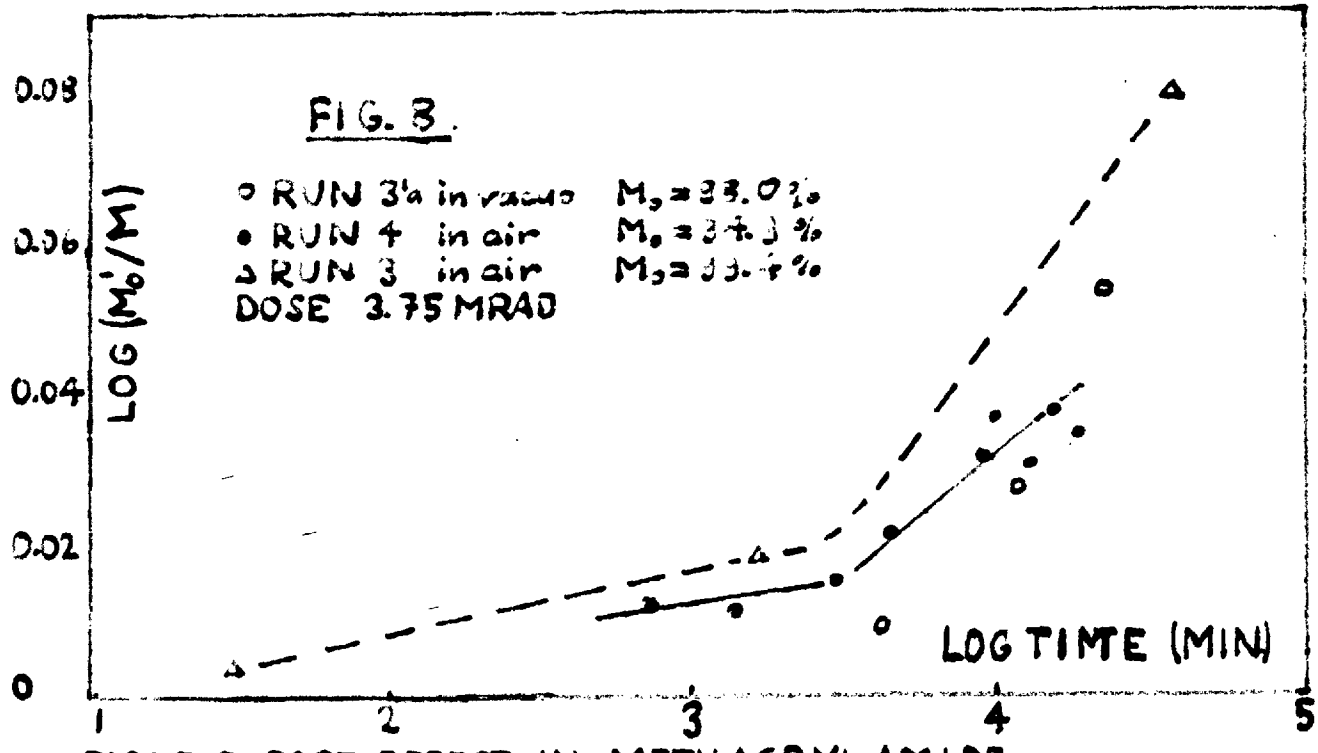
[17b] $\log M_0/M = k_p/k_t \cdot \log (1 + k_t R_0 t)$

For values $k_t R_0 t \gg 1$, the slope of the curve in a log-log plot is

[18] $$\frac{\log (M_0/M)}{\log (k_t R_0 t)} = k_p/k_t$$

If the slopes for different values of $R_0 = kIt$ are the same, then the rate of bimolecular chain termination is independent of the dose. As Figs. 7 and 8 show, this is not the case, i.e., the slope is dependent on R_0 and therefore on the dose, as has been found for acrylamide by Morawetz.[53b]





FIGS. 7, 8. POST-EFFECT IN METHACRYLAMIDE
DOSE RATE 0.04 MRAD/HR.

Our result is partly in agreement with the findings of Baysal et al.[53c] and of Morawetz,[53b] who have found from ESR measurements, that the radical concentration $[\bar{R}]$ decays much more slowly than the polymerization rate, and that $[\bar{R}]$ is a function of the radiation dose. This leads to a different kinetic scheme:

$$-dM/dt = k_p[\bar{M}][\bar{R}_0] \quad [19]$$

, which on integration becomes:

$$\log(M_0/M) = \frac{k_p[\bar{R}_0]t}{2.303} \quad [20]$$

In a plot of log (M_0/M) versus t, the slope of the curve is $k_p[\bar{R}_0]/2.303$. For acrylamide, Baysal found a linear relationship up to a dose of 2.0 Mrad. Since the value of $[\bar{R}_0]$ depends on the total dose, a plot of the slope for different doses versus the dose, should give a straight line, and this Baysal observed.

It is more difficult to draw any firm conclusions from our results in Figs. 9 and 10, as we have reason to believe that oxygen deactivates the growing chains. The main result from Figs. 9 and 10 is the fact that the polymerization rate decreases over a period of 600 hours. The forms of the curves are very similar, whether the irradiation has been carried out <u>in vacuo</u>

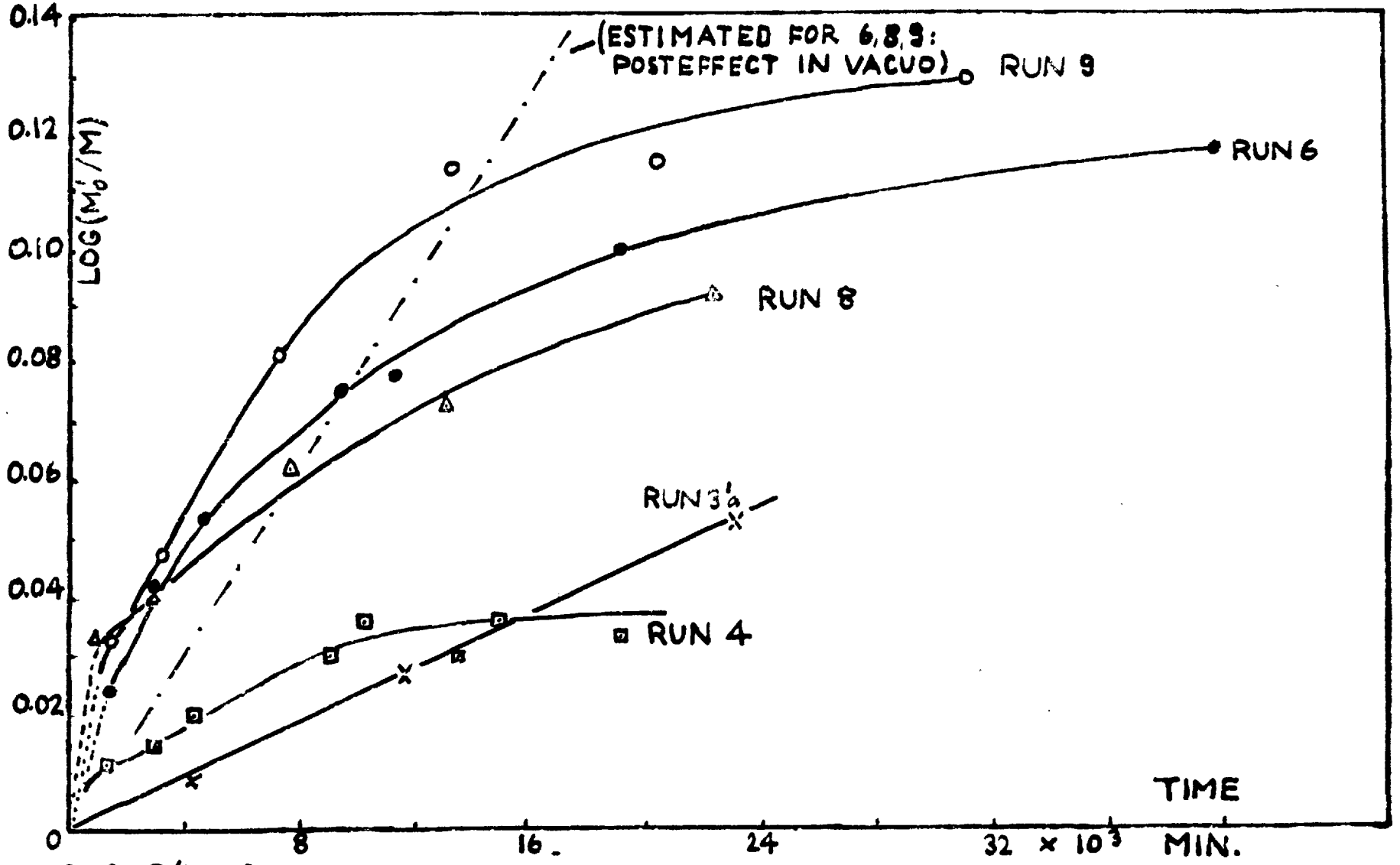


FIG. 9/10. POSTEFFECT IN METHACRYLAMIDE
(DETAILS ON THESE RUNS p.48).

or in the presence of air. We suggest that oxygen has been consumed by reaction with growing chains before the end of the irradiation.

A comparison of the slopes of curves in Figs. 9 and 10 shows, that they are a linear function of the dose (Fig. 11). This suggests, that eq. [20] gives a true picture of the kinetics of the post-polymerization of methacrylamide, within the chosen reaction conditions (oxygen excluded, post-polymerization time as given in Figs. 9 and 10).

Influence of oxygen

A comparison of the values for conversion in Table 8 (25b versus 27a; 27b versus 26) shows, that in the presence of oxygen, the rate of the post-polymerization decreases faster than *in vacuo*. The difference in rate is of the order of 30-40%. Further evidence can be seen in Fig. 10. For samples of the series 3a, which have been kept sealed for different periods of time, the linear relationship [20] is established up to at least 400 hrs. In the samples of series 4, which were opened immediately after irradiation and then kept in a desiccator, a rather short acceleration effect seems to occur initially, followed by a short

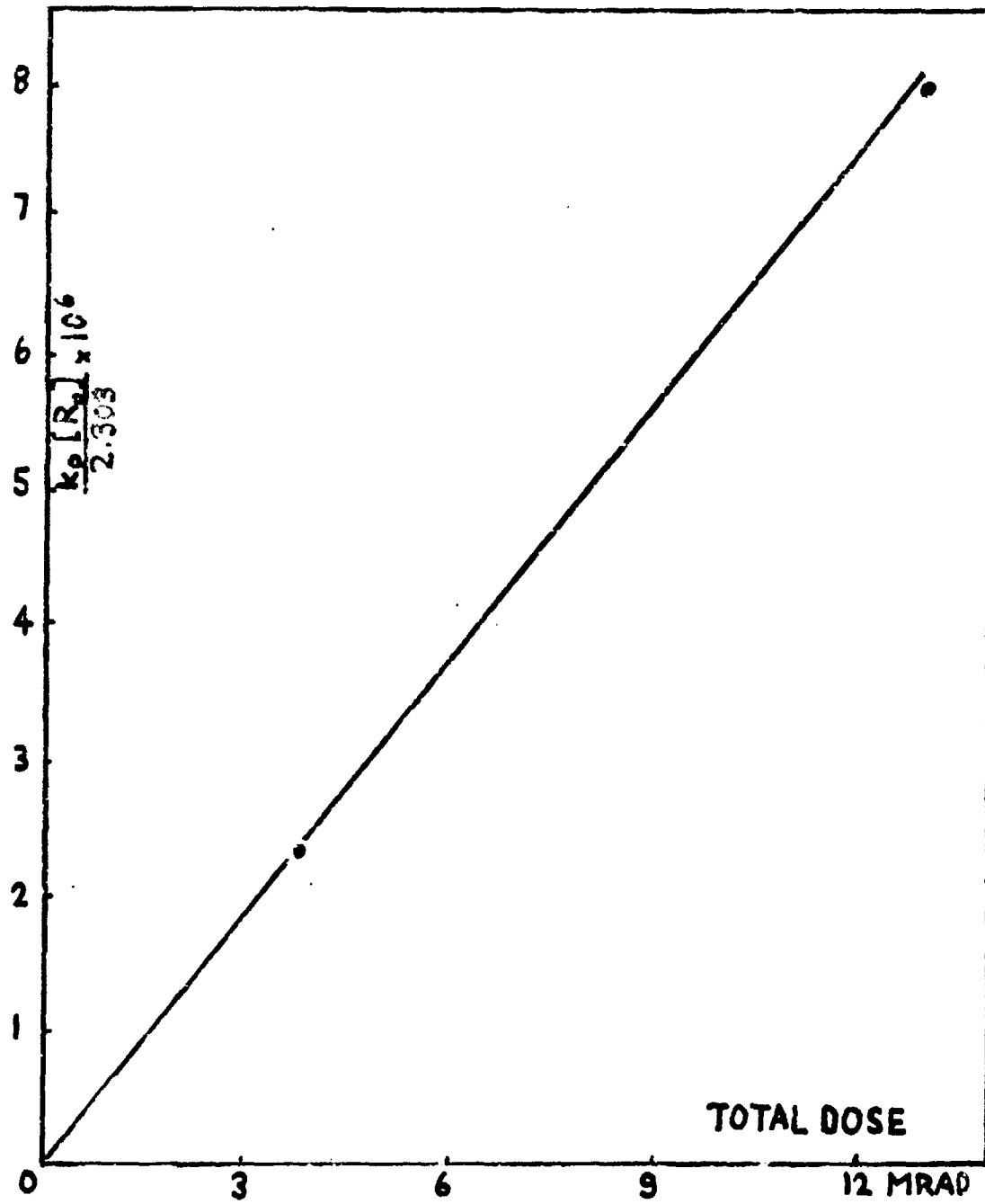


FIG. 11. SLOPES OF METHACRYLAMIDE POLYMERIZATION CURVES FROM FIG. 9/10 VERSUS TOTAL DOSE.

period (ca. 120 hrs.) where the reaction follows eq. /20/. After a total time of about 170 hrs., the curve is flattening out, presumably due to the reduction in the number of growing chains by interaction with oxygen.

It is generally known that oxygen acts as an inhibitor in free radical polymerizations. The rate of the reaction of radicals formed in a crystal, with oxygen, would be expected to be essentially determined by the rate of oxygen diffusion. The peroxyl radical may or may not react further in a more or less complicated reaction sequence. As we irradiated all samples either in vacuo or together with only a small volume of air, the highest peroxyl concentration expected would be of the order of 10^{-2} - 10^{-3} M, a concentration which cannot readily be detected by infrared spectroscopy. More detailed information is available from ESR measurements on irradiated polymers. Schneider et al.[62] and Combrisson and Uebersfeld[63] noted, that the decay of the ESR spectrum of irradiated polymethylmethacrylate was accelerated by the exposure to the atmosphere, and it must be concluded that the peroxyl radical decomposes rapidly in this case. Abraham and

Whiffen[24] found a rapid "build up" of peroxyl radicals in samples of high density polyethylene which had been irradiated *in vacuo* and were then exposed to air. Ballantine[64] et al. found no peroxyl radicals in a similar experiment with low density polyethylene. A detailed study of graft co-polymerization following a pre-irradiation method (in air or *in vacuo*) has been made by Shinohara and Tomioka.[65] These authors showed that free radicals in polyethylene disappear in the presence of air monomolecularly, and that the decay rate is a function of the temperature. Good agreement was found between the number of trapped free radicals and the experimentally determined rate of reaction with a number of vinylic monomers.

5. Polymerization of N-Arylmethacrylamides.

In the last few years, a series of N-arylmethacrylamides have been prepared and polymerized. We have prepared a number of solid compounds in this series, irradiated them *in vacuo* with γ-rays and isolated any polymer formed by precipitation into methanol. We have also polymerized some of these monomers in solution, using a free radical initiator. The infrared

spectra of monomers and polymers have been taken* and are discussed in connection with monomer structure and monomer reactivities.

5.1 Experimental

5.1.1. Preparation of N-Arylmethacrylamides (Table 9) [I, 6-13]

Methacroylchloride was prepared from methacrylic acid and benzoylchloride.[66] A pure product was obtained; b.p. 96-100° (Lit: 95-96°); n_D^{15} 1.4410 (Lit: n_D^{20} 1.4435). The aromatic amine (0.2 mole) was stirred with water (50 ml.) in a two-necked, round-bottomed flask, fitted with a stirrer and a dropping funnel. Freshly distilled methacroylchloride (0.1 mole) was added dropwise with very vigorous stirring over a period of about 90 min. to the emulsion or suspension of the amine in water. At the end of the addition, the mass was acidified with hydrochloric acid until Congo red paper gave a blue colour, and then stirred for another half hour. Solid N-substituted methacrylamide was filtered off, washed with water until neutral and dried over phosphorous pentoxide in a vacuum desiccator. If the reaction product did not precipitate as a solid, it was extracted

* see Appendix I

with ether. The ether solution was thoroughly washed with aqueous sodium carbonate, water, hydrochloric acid and water and dried over sodium sulphate. After removing the solvent, crude products were obtained. All products were purified by treatment with charcoal, recrystallization from hot petrol or from aqueous ethanol, or distilled under high vacuum.

5.1.2. Polymerization in solution, initiated by benzoyl peroxide (III, 1 - 15, Table 10)

Monomer (20 g.) was dissolved in a suitable solvent, dry benzoyl peroxide (0.5 %) added, the solution de-aerated in a pyrex-glass tube and sealed under vacuum. The samples were heated at 60-62° for several hours, cooled and the polymer precipitated into methanol. In some cases, the methanol was removed under vacuum and a further fraction of polymer was obtained by precipitation into diethyl ether. The polymer was separated by centrifugation, washed with methanol, dissolved in dioxane and freeze-dried on a high vacuum line.

5.1.3. Polymerization in the solid state, initiated by γ-rays (Table 11) (II, 57-65, 70,73, 77, 78)

Monomer samples (1-3 g.) were dried in pyrex-glass tubes on a high vacuum line and sealed under vacuum.

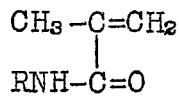
The irradiations were carried out at room temperature, using a dose rate of 0.039 Mrad/hr. After irradiation, the tubes were broken, and a weighed amount of irradiated monomer thrown into methanol. Any polymer formed was separated by centrifugation, washed with methanol and freeze-dried from dioxane.

During irradiation, some of the monomers became coloured. The colour was stable in air for several weeks, but faded within a few minutes on addition of methanol.

5.1.4. Viscometry of polymer solutions

Attempts have been made to determine the intrinsic viscosity $[\eta]$ of solutions of some of the polymers obtained by different techniques. Preliminary experiments showed, that these solutions behaved like polyelectrolyte solutions (viscosity increasing with dilution); this is ascribed to a partial hydrolysis of the polymers during preparation and purification. Some microanalytical data support this view. Due to the small amount of "irradiation-polymer" available, these experiments - aimed at an estimation of the molecular weight of the polymers - had to be given up.

Table 9. N-Arylmethacrylamides



R	m.p. (°C) found	m.p. (°C) Lit.	Yield %	IR	Anal.
Phenyl	84-85	85[a,c]	83	29	18
o-Tolyl	94.5-95	94-95[a-c]	82	31	20
m- "	79-80	78-78.5[b]	87	33	22
p- "	88.5	88.88.5[b]	80	32	21
o-Ethoxyphenyl	45-46	44.5-46[c]	72	27	16
m- " "	95-96	95.5-96[b]	34	37	26
p- " "	108-109	107.5[b]	55	28	17
o-Chlorophenyl	59-60	57[b]	41	34	23,29
m- " "	105-106	105-105.5[b]	67	36	24
p- " "	113-114	112-112.5[b]	43	35	25
o-Bromophenyl	47-48	-	80	60	43/60
o-Carboxyphenyl	175-176	169-170[d]	24	58	41
o-Methoxyphenyl	b.p.$^{0.5}$	130-2	80	59	44
α-Naphthyl	118-119.5	111-112[a]	38	55	39/51
β- "	144-145	138-139[a]	31	56	40
-N-(methyl)(phenyl)	58	60.5-61[b]	87	30	19

[a] Patai et al., J. Amer. Chem. Soc., 1952, 74, 845.

[b] Sokolova et al., Zhur. obschei Khim., 1957, 27, 2205 C.A. 1958, 52, 6228

[c] Sokolova et al., Zhur. obschei Khim., 1958, 28, 779

[d] Koton et al., Zhur. obschei Khim., 1957, 27, 2233 C.A. 1958, 52, 6228.

Table 10. Polymerization of N-Arylmethacrylamides

(III, 6 - 15)

R	Solvent	monomer %	conversion %	IR. no.	Anal. no.
II	benzene	20	-	-	-
III	"	20	22	64	48
IV	"	20	21	-	45
V	"	20	33	62/63	46/47
VI	"	20	19	65	50
VIII	A	10	40	66	49
IX	benzene	13	60	67	52
X	B	13	9	68	53
XI	B	13	50	71	54
XII	benzene	20	83	72	58
XIII	cyclohexanone	11.5	70	75	59
XIV	"	16	27	74	57
XV	"	20	75	-	56
XVI	benzene	18	56	73	55

sample III heated at 61° for 48 hrs.

samples II, IV-VIII heated at 60° for 42 hrs.

samples IX-XIV heated at 62° for 42 hrs.

A: solvent mixture 75% benzene + 25% cyclohexanone

B: " " 66% " + 34% "

Table 11 Irradiation of N-Arylmethacrylamides

/II, 62-66, 70, 73, 77, 78/

	R	Irrad. No.	Dose Mrad	Conversion %
I	phenyl	17	24.2	-
II	(phenyl) (methyl)	18	24.2	-
III	o-Tolyl	19	24.0	-
IV	m- "	20	24.0	-
V	p- "	21	24.0	-
VI	o-Ethoxyphenyl	22[a]	24.0	3.0
		32	23.8	2.4
VII	m- "	23[b]	24.0	5.6
		33	24.8	0.95
VIII	p- "	24	24.0	-
IX	o-Chlorophenyl	29[a]	40.7	11.0
		29[b]	25.9	5.3
X	m- "	30	24.8	-
XI	p- "	31	24.8	-
XII	o-Bromophenyl	46[d]	27.4	5.1
		-	40.7	9.0
		-	15.0	4.1
XIII	o-Carboxyphenyl	45	27.4	-
XIV	α-Naphthyl	48	27.4	-
XV	β- "	47	27.4	-
XVI	o-Methoxyphenyl	-	-	-

[a] IR 43; Analysis 30/32

[b] IR 44; Analysis 31/33

[c] IR 81;

[d] IR 69;

5.2. Results and Discussion

The main results of the peroxide initiated polymerizations are summarized in Table 10.

The peroxide initiated polymerization in bulk and in solution was first reported by Patai et al.[67] They obtained polymers from V and XIII, but found - in contradiction with our results - no polymers in experiments with I, III, IV and XVI.

Sokolova et al.[68-71] investigated the polymerization of N-chlorophenyl-, N-ethoxyphenyl- and N-carboxyphenyl-methacrylamides in bulk and in solution. Our results are in agreement with their findings. Whereas methacryloylanilide and methacryloylmethylanilide could not be polymerized under the chosen reaction conditions, substituted N-phenylmethacrylamides reacted to give high polymers in reasonable yields. Sokolova found that the polymerization rate in these compounds decreased in the order ortho isomers > meta isomers > para isomers. The same order was found to hold for the molecular weights of the polymers obtained. As the results of polymerizations in solution depend on the solvent, our results cannot be discussed in detail; the main purpose of our experiments was to obtain polymers for comparison with our polymeric irradiation products.

On irradiation, methacrylanilide and methacryl-N--methylanilide did not give any polymeric product. This radiation resistance, compared with methacrylamide, might be discussed as just another example of the radiation resistance of compounds containing an aromatic nucleus.* Our unsuccessful attempts to obtain polymers by irradiating solid N-tolyl-methacrylamides may be similarly explained.

It was therefore somewhat surprising to get polymer from some other o or m-substituted phenylmethacrylamides (Table 12).

Table 12

Irr.		Dose Mrad	Conversion %	G "apparent"
29	o-Chlorophenyl-M	40.7	11.0	13.3
-	"	25.9	5.3	9.6
-	o-Bromophenyl-M	15.0	4.1	11.8
46	"	27.4	5.1	7.3
-	"	40.7	9.0	9.1
22	o-Ethoxyphenyl-M	24.0	3.0	5.0
32	"	23.8	2.4	4.7
23	m-Ethoxyphenyl-M	24.0	5.6 (?)	11.0
33	"	24.8	0.95	1.8

* see section 1.4.

The conversion rate is low, and so are the "apparent" G-values. They are within the range of G-values for polymer formation from some liquids, as quoted by Charlesby.[21]

	G(polymer)
Cyclohexane	2.6 - 6.3
Benzene	0.59
Toluene	0.9 - 2.16
Styrene	0.52 - 1.27
Chlorobenzene	6.1 - 14.6

It can be seen, that substitution on the benzene ring leads to a higher radiation sensitivity. This might suggest that the polymer formation in our experiments was due to random cross-link formation between neighbouring monomer molecules in the crystal lattice.

We have compared the infrared spectra of the polymer pairs prepared by free radical initiation and by irradiation and found, that the two spectra are in all examples virtually identical; i.e. in both cases the polymer consists of an aliphatic main chain, carrying the aromatic side groups.

The singular reactivity of some ortho-substituted arylmethacrylamides under the influence of γ-radiation

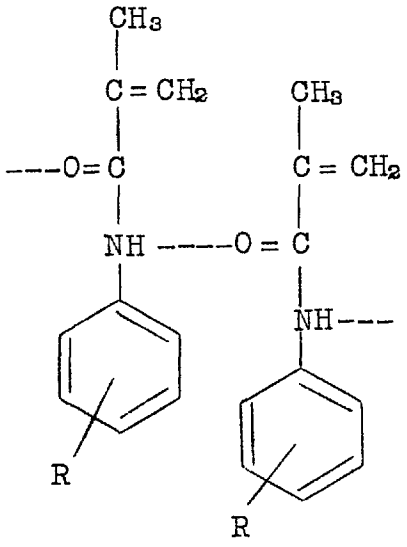
is another interesting feature. A similar situation arises in solution and in the molten state, as has been reported by Sokolova et al.[68-71] They showed from infrared spectra of monomers, that some ortho--substituted arylmethacrylamides (o-Cl, o-COOH, o-COOR, o-phenyl) show only weak, or even no, hydrogen bonding between neighbouring amide groups, whereas all investigated meta or para substituted monomers show marked hydrogen bonding in the solid state and - with one exception - even in the melt. We have checked our infrared spectra and can confirm these findings (Appendix II).

We found, that o-bromophenylmethacrylamide and o-methoxyphenylmethacrylamide also have free amide. o-Tolylmethacrylamide, on the other hand, shows only bonded amide in the solid state.

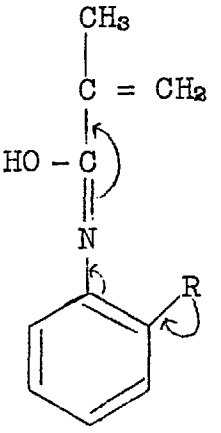
Sokolova et al.[68-71] concluded from their results, that in bulk polymerization, all monosubstituted phenylmethacrylamides showing free amide groups in the infrared spectrum, polymerize faster than the corresponding non-bonded monomers. Our results show, that this statement holds also for methacryloyl toluidides; we would like to suggest, that this rule is

also valid for the γ-ray initiated solid state polymerization of a group of these compounds.

The Russian workers[68-71] suggested, that the inhibition effect of these hydrogen bonds may be due to steric reasons or to the loss of double bond character of the carbon-oxygen bond (I). As the reactivities of <u>ortho</u> and <u>para</u> substituted methacrylanilides are found to be completely different, any activation or deactivation of the vinyl bond due to resonance forms of (II) seems improbable. This is also supported by the virtually invariable position of the δ=C-H absorption band (Appendix II).



(I)



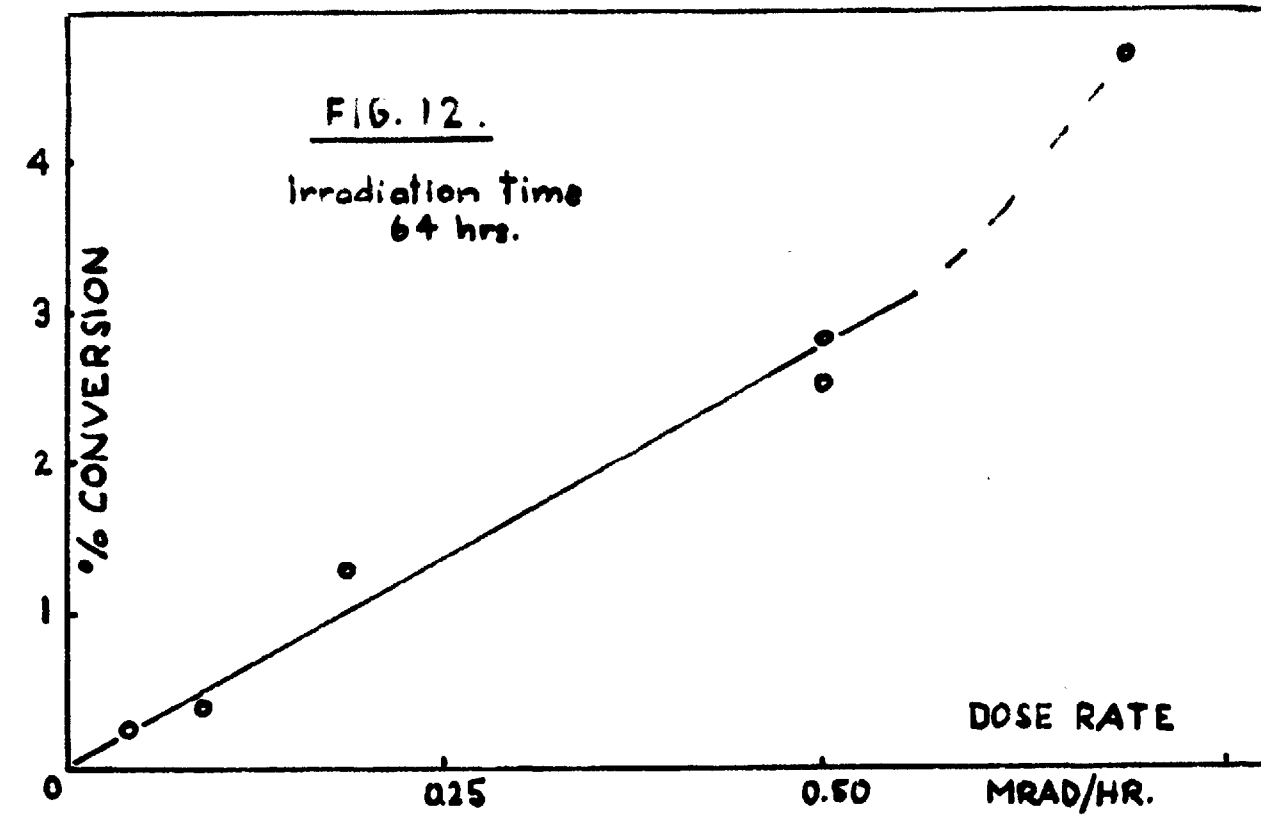
(II)

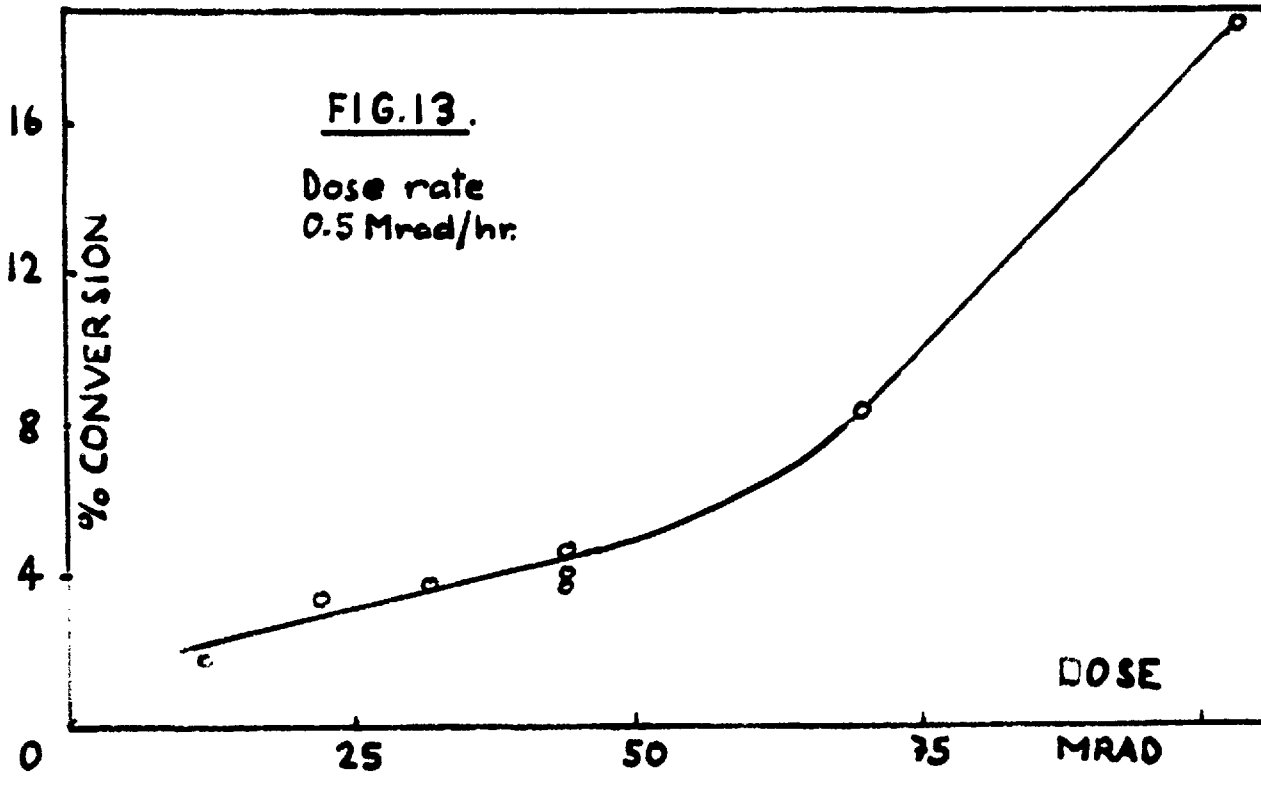
5.3. Polymerization of o-ethoxyphenylmethacrylamide (II, 73-75) (Figs. 12,13)

The rate of the in-source polymerization of o--ethoxyphenyl methacrylamide was found to be a linear function of the dose rate for intensities between 0.04 Mrad/hr. and 0.7 Mrad/hr. (Fig. 12), up to a conversion of ≈ 3%. The monomer conversion is also a linear function of the dose up to ≈ 5% conversion (Fig. 13). At this point a sudden rate increase occurs, as has been found for acrylamide[50] and methacrylamide (Figs. 1-4). This acceleration effect seems to be a common feature of this type of solid state polymerization.

5.4. Influence of the monomer lattice on the solid state polymerization

The stereospecific decomposition of choline chloride has been mentioned in section 2.2., and the remarkable difference in the reactivity of acrylic acid salts can be seen from Table 4; potassium acrylate polymerizes rapidly at 0°C, while the sodium and lithium salts react at comparable rates only at 110°C and 150°C, respectively.[72] The stereospecific





IN-SOURCE POLYMERISATION OF
METHACRYLOYL-ortho-PHENETIDIDE

polymerization of several monomers as clathrate compounds with urea and thiourea has been induced by high energy radiation.[73-75]

It was hoped to obtain stereospecific polymers from solid state polymerizations, where the reaction might take place within the crystal lattice of the monomer and might be directed by it. The alternative would be a two phase mechanism. According to this concept, the reaction proceeds at different sites within the crystal. After the first few reaction steps, regions of pure polymer imbedded in pure monomer are formed. Further reaction would take place at the interface of the two. The polymer and monomer regions would remain segregated until the crystal is completely polymerized.

Adler and Reams[76] obtained a series of X-ray diagrams from irradiated single crystals of acrylamide at various stages of polymerization. They were able to show that even at low conversions, a steady decrease in the intensity of the monomer pattern occurs, and that no new reflections, due to crystalline polymer, occurred. A slight broadening of the monomer diffraction patterns was tentatively ascribed to strain

within the monomer. This result was taken to mean, that the reaction proceeds by a two-phase mechanism in which the polymer exists as a separate phase throughout most of the reaction.

Baysal et al.[53c] provided evidence of a different kind in support of this view. They assume that while the radiation is adsorbed uniformly by the acrylamide crystals, there is produced a non-homogeneous distribution of reactive growing chains which, on the basis of ESR data, are believed to be free radicals. As we have noted for high density polyethylene,[24] potentially reactive sites are trapped in the more perfect regions of the lattice. The favourable sites for nucleation of the reaction are areas with imperfections. As the reaction proceeds from the strained and imperfect regions, additional strain can then release the dormant radicals by providing an environment favourable for propagation. This would account for the increase in the efficiency factor in eq. [12] and the acceleration in rate of conversion in Figs. 3 and 4.

This strain hypothesis is supported by results obtained from mixed crystals[53c]. The addition to

acrylamide of isomorphous propionamide as diluent should introduce more imperfections and should produce a higher rate of reaction than in pure acrylamide; this has been demonstrated.

All polymers produced so far by solid state polymerization appear to be amorphous. Our own experiments showed that this is the case for poly-methacrylamide and for poly-(o-bromophenyl)methacryl-amide.

6. Irradiation of substituted styrenes

The radiation-induced liquid phase polymerisation of styrene has been intensively studied.[26] Chapiro and Stannett[55] reported the radiation induced post--polymerisation of styrene in the solid state, and Lowry[77] irradiated α-methylstyrene with γ-rays. No results on the radiation-induced polymerization of nuclear-substituted styrenes have been published.

We prepared a number of substituted styrenes (α-methyl-, o-nitro-, m-nitro-, p-nitro-, m-amino-, p-amino-, p-dimethylamino-, and p-methoxystyrene; p-vinylbenzoic acid, p-vinylbenzoic acid methyl ester) and irradiated them in the solid state. All polymers

obtained were compared with corresponding samples obtained by conventional methods. The results will be discussed in connection with polymerization mechanisms.

6.1. Polymers of substituted styrenes

α-Methylstyrene belongs to a small group of vinylaromatic compounds which may polymerize by three different mechanisms. Cationic polymerization[78,79] using catalysts of the Friedel-Crafts type (e.g. $AlCl_3$, BF_3) is the most frequently used method; the reaction proceeds with increasing rate at low temperatures down to -130° (in ethyl chloride). The products are high polymers, and are under certain conditions crystalline.

Anionic polymerization at room temperature has been investigated by Jones,[80] using dry, air-free monomer and finely divided sodium. A more detailed account of the anionic polymerization has been given by Sirriani;[81] he found that the polymerization of α-methylstyrene in tetrahydrofuran at -78°, using sodium naphthenide as a catalyst, yields a practically monodisperse polymer, i.e., a polymer with a very narrow molecular weight distribution.

The free radical initiated polymerization of α-methylstyrene proceeds at a low rate. Sapiro, Linstead and Newitt[82] obtained polymer with a molecular weight of ca. 5600 in 85% yield by heating the monomer under high pressure at 100°. Schildknecht[83] and Lowry[77] mentioned a slow photopolymerization at room temperature leading to polymer of low molecular weight. Emulsion polymerization using cumene hydroperoxide as a catalyst proceeded at a slightly higher rate and led to polymers with a molecular weight of ca. 50000. Irradiating monomer with γ-rays[77] (dose rate 0.58 Mrad/hr.) at 30° gave polymer with a rate of 0.0057% /hr.

Poly-(nitrostyrenes) are usually obtained by nitration of polystyrene. The polymerization of o-nitrostyrene has been unsuccessfully attempted, using benzoyl peroxide and borum trifluoride as catalysts.[84] Poly-(m--nitrostyrene) has been obtained by Matsui[85] by heating the monomer for 48 hrs. at 165-170°. A dark-brown, brittle polymer (D.P. 53) was obtained. Marvel et al.[86] found no polymer on heating m-nitrostyrene in bulk with benzoyl peroxide or on irradiation with UV--light. The attempted polymerization of an emulsion

with potassium persulphate as initiator was equally unsuccessful. Smets and Rickens[87] obtained with benzoyl peroxide low molecular products (M.W. 750). Wiley and Smith[88] found under similar conditions an equivalent result. They obtained with borum trifluoride or aluminium chloride a brittle solid in good yield (M.W. 870); an emulsion polymerization with potassium persulphate gave a product with a molecular weight of 3600. The polymerization of p-nitrostyrene has been reported by Basler[89], Strassburg et al.[90] and Wiley and Smith.[88] Brittle polymers have been obtained in experiments with benzoyl peroxide and with persulphate. The low reactivity of p-nitrostyrene may also be seen from co-polymerization data with styrene and with methyl methacrylate.[91]

Poly-(aminostyrenes). Only little information on poly-(aminostyrenes) could be found in the literature. Matsui[85] obtained a colourless, insoluble solid on heating m-amino-styrene for 16 hrs. at 165-170°. p-Dimethylamino-styrene was polymerized[86] by heating in a test tube at 120° for 24 hrs. The product had M.W. 1620. On polymerizing with benzoyl peroxide in dioxane solution, a gum was obtained. Wiley and Schmitt[92] prepared a series

of cross-linked p-dimethylaminostyrene - styrene co-polymers, which on quaternization with methyl iodide gave ion exchange resins with a uniform distribution of charge.

Poly-(p-methoxystyrene) has been previously obtained by free radical initiated polymerization[93-95] and by cationic polymerization,[96] using $SnCl_4$ as a catalyst (D.P. 800).

p-Vinylbenzoic acid was polymerized thermally[97] at 100°. The product had M.W. 4700; (and) its methylester at 100--130°.[97-99] The product had M.W. 45000. Both polymers were clear and had the highest softening points, 350° and 205-212° respectively, of all polymers described in this section.

6.2. Preparation of monomers

p-Nitrostyrene

p-Nitrophenylethylbromide[100,90] (I, 30). - A mixture of acetic anhydride (100 g.) and glacial acetic acid (60 g.) was chilled to 0° in a 500 ml. three-necked flask with stirrer, thermometer and dropping funnel. After adding slowly fuming nitric acid (63 g.) the mixture was chilled to -5°. Phenylethylbromide (93 g.) was dropped

slowly into the reaction mixture, while the temperature was kept below 0° by adding solid carbon dioxide. The white precipitate (Fr. 1) was filtered off on a glass filter at 0°, washed with water and recrystallized from benzene-petrol (1:5) at 0° to give white prisms (37.5 g.), m.p. 64-65° (Lit.[90] 69-70°) : Fr. 1'. The mother liquor of Fr. 1 was extracted with benzene, washed with water until the filtrate gave a neutral reaction, combined with the mother liquor of Fr. 1' and gave on distillation a second fraction (17.5 g.), b.p. 139-50/2 mm. which melted at 63-65° after recrystallization. The total yield of pure <u>para</u> isomer was 51.5 g. Low boiling oils (47.5 g.) consisted mainly of the <u>ortho</u> isomer.

<u>p-Nitrostyrene</u>[90] (I, 32). - <u>p</u>-Nitrophenylethylbromide (5 g.), triethanolamine (50 g.) and water (30 ml.) were heated in a 100 ml. round bottom flask equipped with a Stark-Dean trap with condenser. The <u>p</u>-nitrostyrene separated as a heavy yellow liquid. After one hour, another 15 g. of the <u>p</u>-nitrophenylethylbromide was added in portions over a period of two hours. The crude product was taken up in petrol and dried over anhydrous sodium sulphate. On recrystallization from petrol (200 ml.) at 0°, 6.8 g. pure <u>p</u>-nitrostyrene was

obtained; m.p. 21°. (Lit: m.p. 21°). (Found: N, 9.21%; calc. for $C_8H_7NO_2$: N, 9.39%).

m-Nitrostyrene (I, 62)

m-Nitrocinnamic acid[101]. - m-Nitrobenzaldehyde (75.5 g.), malonic acid (57.5 g.), 95% ethanol (125 ml.) and pyridine (12.5 ml.) were gently refluxed on a steam bath for 7 hours. After cooling to 0°, the crystals formed were collected on a Buchner funnel, washed with cold ethanol (50 ml.) and two 50 ml. portions of cold diethyl ether. The crude product was suspended in ethanol (150 ml.) and digested on a steam bath for 3 hours. The mixture was cooled, and the crystals filtered and air-dried. 68.5 g. of pure light yellow m--nitrocinnamic acid was obtained; m.p. 195-196° (Lit.: m.p. 200-201°).

m-Nitrostyrene[101,84]. - m-Nitrocinnamic acid (30 g.), copper powder (3.5 g.) and dry, purified quinoline (60 ml.) were heated to 185-198° in a two-necked flask, equipped with an air condenser and a thermometer, during which time a steady stream of carbon dioxide was evolved. After 3 hours, the reaction mixture was cooled and

poured into a mixture of concentrated hydrochloric acid (75 ml.) and ice (175 g.). The m-nitrostyrene was isolated by steam distillation, approximately 1 l. of distillate being collected. The distillate was extracted with three 50 ml. portions of chloroform, and the solution dried over anhydrous sodium sulphate. A Claisen flask equipped with a dropping funnel was heated on a steam bath, and the chloroform solution was added dropwise. The residue was then distilled under reduced pressure. Pure m-nitrostyrene (8.3 g.) was obtained b.p. 104-105°/1.5 mm.; n_D^{21} 1.5822 Lit.: n_D^{20} 1.5836 (Found: N, 9.64%; calculated for $C_8H_7NO_2$: N, 9.39%).

o-Nitrostyrene

o-Nitrocinnamic acid ethyl ester[102] I, 66). - Nitric acid (d 1.5; 500 g.) was cooled to 0° in a 1 l. three-necked flask equipped with stirrer and thermometer. Under vigorous stirring, cinnamic acid (105 g.) was added over a period of 1 hour, the temperature being kept at -5° to 0°. After the end of the addition, stirring was continued for another 10 min. The reaction mixture was poured into ice-water, the solid filtered off, washed with ice-water and dried under vacuum

on a steam bath. The crude product (132 g.) was suspended in 650 ml. of ethanol and the hot suspension saturated with dry gaseous hydrogen chloride until all material was dissolved. The mixture was cooled under an atmosphere of hydrogen chloride gas. The crystals formed were filtered, washed with ice-cold ethanol and dried. On concentrating the solution, another small fraction of p-nitrocinnamic acid ethyl ester was obtained; this para isomer melted at 138-139°. (Lit. 138°). The mother liquor was further concentrated, taken up in ether and washed several times with sodium bicarbonate solution, then with water. The ether solution was dried, the solvent distilled off and the solid obtained recrystallized from ethanol. The spectroscopically pure o-nitrocinnamic acid (14.3 g.) melted at 44-45° (Lit. 42°).

o-Nitrocinnamic acid[102] (I, 69). - o-Nitrocinnamic acid methyl ester (20 g.) was refluxed for 2 hours with 4 N hydrochloric acid (350 ml.) and glacial acetic acid (30 ml.). The precipitate was filtered off and digested on a steam bath with ethanol (50 ml.). The pure acid melted at 240-42° (Lit.: 240°).

o-Nitrostyrene[84] (I, 69). - The same method as for the preparation of m-nitrostyrene was used. The reaction

mixture was heated for 4 hours at 170-180° and for one further hour at 190-200°. The crude product gave on distillation a yellow oil, b.p. 104-106°/0.8 mm., n_D^{21} 1.5784; m.p. 13-14° (Lit.: m.p. 13-14°). (Found: C, 64.57; H, 4.42; calculated for $C_8H_7NO_2$: C, 64.42; H, 4.74).

p-Dimethylaminostyrene[86] (I, 54). - A solution of p-dimethylaminobenzaldehyde (25 g.) in dry ether (600 ml.) was added dropwise to a cooled solution of methyl-magnesium iodide (prepared from 5 g. of magnesium) in ether (250 ml.). After the end of the addition, the mixture was kept standing for 20 min., then 100 ml. saturated ammonium chloride solution, containing 5 ml. concentrated hydrochloric acid, was added dropwise. The ether layer was separated and the aqueous phase extracted with two 100 ml. portions of ether. On removal of the ether, solid yellow p-dimethylaminophenyl methyl carbinol was obtained, which gave on distillation under reduced pressure, water and p-dimethylaminostyrene. The crude product was taken up in ether, dried and gave on distillation a practically colourless liquid, b.p. 90-91°/2.5 mm.; $n_D^{22.5}$ 1.6096 (Lit. n_D^{20} 1.6110,[77] 1.6010[81]) (Found: N, 9.80%; calculated for $C_{10}H_{13}N$:

N, 9.52%). On further heating, the main amount of the residue distilled as second fraction at 236-240°/ 2.2 mm., and was found to be a dimeric product. (Molecular weight found 294.2; calculated for $(C_{10}H_{13}N)_2$:292)

p-Vinylbenzoic acid (I, 56)

p-Acetylphenylethyl bromide[100]. - A solution of phenylethyl bromide (46.6 g.) in benzoyl chloride (40 ml.) was added dropwise under vigorous stirring to a cooled mixture of aluminium chloride (44.4 g.), benzoyl chloride (20 ml.) and carbon disulphide (150 ml.). After all had been added, stirring was continued for one hour at 0° and then for five hours at room temperature. The solution was stirred into a mixture of ice and concentrated hydrochloric acid, the carbon disulphide layer separated and the water phase extracted twice with benzene. The combined benzene-carbon disulphide solution was washed with 2N hydrochloric acid, water, 2N sodium hydroxide and with water. The solvents were distilled off on a steam bath. The pure product (48.75 g.) distilled at 134-137°/1 mm.; n_D^{19} 1.5742 (Lit.: b.p. 117-118°/0.1 mm.; n_D^{25} 1.5724).

p-Carboxyphenylethylbromide[100]. - p-Acetylphenylethyl bromide (23 g.) was added dropwise under stirring

to a cooled (0°) alkaline hypobromite solution prepared from bromine (48 g.), sodium hydroxide (33 g.), water (280 ml.) and dioxane (200 ml.). Stirring was continued for another three hours at 0°, the solution acidified with excess hydrochloric acid and the precipitate filtered from the bromoform and water. The solid was washed with water and dried in a vacuum desiccator over calcium chloride. The crude product (15 g.) was recrystallized from benzene to give pure p-carboxyphenylethyl bromide (13.1 g.), m.p. 209-210° (Lit. 205-207°).

p-Vinylbenzoic acid[97] (I, 73). - Pure p-vinylbenzoic acid (m.p. 143-144°) has been prepared previously from p-cyanostyrene[97]. A product obtained by Bissel et al.[103] (m.p. 123-128°) from p-(α-bromoethyl)benzonitrile seems to have been impure.

A suspension of p-carboxyphenylethyl bromide (7.5 g.) potassium hydroxide (7 g.) and hydroquinone (50 mg.) in ethanol (50 ml.) was gently refluxed for one hour. After cooling to 0°, the solid was filtered off, washed with ice-water (10 ml.) and, dissolved in water (50 ml.) at 25°. The solution was acidified with concentrated hydrochloric acid, and the precipitated acid filtered off, washed with ice-water (10 ml.) and dried at room

temperature under vacuum (0.05 mm.). The crude product (4.9 g.) was dissolved in hot aqueous ethanol and treated with charcoal. On cooling, pure p-vinylbenzoic acid (4.15 g.) crystallized in fluffy plates; m.p. 140-141°. The analytical sample was slowly sublimed at 10^{-2} mm. Hg at 80-90° (Found: C, 72.14%; H, 5.41%; calculated for $C_9H_8O_2$: C, 72.97%; H, 5.44%).

p-Vinylbenzoic acid methyl ester[97] (I, 74). - p-Vinylbenzoic acid (3.0 g.) was dissolved in 5% methanolic hydrochloric acid (40 ml.), cooled in an ice-bath and kept at 0° for 24 hours. The solution was concentrated under vacuum (0-10°), to a volume of ca. 10 ml. and the precipitate formed (0°) was filtered and recrystallized twice from aqueous ethanol, containing a trace of hydroquinone. The ester was dried in a vacuum desiccator over phosphorous pentoxide; the analytical sample was dried for six hours at 10^{-3} mm. (20°) and melted at 34.5-35.5° (Lit.: 35.5 - 36.5°) (C, 73.92%; H, 6.17%; calculated for $C_{10}H_{10}O_2$: C, 74.05%; H, 6.22%).

m-Aminostyrene[104] (I, 71). - A solution of m-nitrostyrene (11.0 g.) in ether (50 ml.) was added in small portions to a suspension of aluminium amalgam (10 g.) in ether (400 ml.) in a 2 l. three-necked flask fitted

with stirrer and condenser. At intervals, water (12 ml.) was added in portions to obtain gentle refluxing. After all the water and nitrostyrene had been added, the mixture was kept standing for 30 min., refluxed for 15 min., cooled and filtered. The precipitate was washed several times with ether and the combined filtrate and washings dried over sodium sulphate. The ether was removed on a steam bath and the residue distilled in presence of hydroquinone (50 mg.). Pure m-aminostyrene (5.7 g.) was obtained; b.p. 94-95°/3 mm.; n_D^{21} 1.6114 (Lit.: n_D^{26} 1.6069). (Found: N, 11.30%; calculated for C_8H_9N: N, 11.76%).

p-Aminostyrene

p-Aminostyrene has been prepared previously by dehydration of β-(p-aminophenyl)ethyl alcohol[105] over potassium hydroxide[106,107]; by reduction of p-nitrostyrene with aluminium amalgam[104]; by reduction of p--aminoacetophenone with lithium aluminium hydride and dehydration of the carbinol formed over potassium hydroxide.[108] The first method involves difficult separations of mixtures; the last in our hands gave p-aminoethylbenzene.

β-(p-Nitrophenyl)ethyl alcohol[105,109] (I, 36). - β-Phenylethyl bromide (75 g.) was added dropwise with continuous stirring to fuming nitric acid (d: 1.5, 300 ml.) at -25° to -20°. At the end of the addition, stirring was continued for another 30 min. at -15°. The reaction mixture was poured on to ice (400 g.) and extracted with ether. The ether extracts were washed with sodium carbonate solution and with water, until the washings had p_H 7. The ether solution was dried and the solvent distilled off. The oil (51.5 g.) obtained was refluxed with 2% methanolic hydrochloric acid for 3½ hours. After removing the solvent, the oily product (57.4 g.) crystallised very slowly at -10 to -15°. The crystals were filtered on a Buchner funnel and the crude product recrystallised from aqueous ethanol. A first fraction (12.4 g.) had m.p. 60-61° (Lit: 62°), a second fraction (18.2 g.) melted at 55-56°.

β-(p-Aminophenyl)ethyl alcohol[105,109] (I, 38). - β-(p-Nitrophenyl)ethyl alcohol (10 g.) was added in portions to a suspension of zinc powder (40 g.) in boiling water (200 ml.) containing calcium chloride (4 g.). After the addition of the nitro alcohol, another portion of

zinc (5 g.) was added, the mixture was kept boiling for another 30 min., filtered and the residue washed with hot water (2x 50 ml.). The filtrate was neutralised with a few drops of sodium carbonate solution, and the hot solution filtered. The coloured filtrate was evaporated to dryness under vacuum and the residue obtained extracted with ethanol (2x 75 ml., 1 x 25 ml.). The extract was concentrated and gave on cooling a first fraction (2.58 g.); m.p. 109-110° (Lit: 107-108°). On addition of water, a second fraction (1.10 g.) was obtained, which melted at 109-110°.

p-Aminostyrene[107]. - A solution of β-(p-aminophenyl)ethyl alcohol in dioxane (80 ml.) was added dropwise to a fused mixture of sodium hydroxide and potassium hydroxide in a copper flask with condenser (18 mm. Hg.) and receiver. The distillate was freed from dioxane by distillation and the residue taken up in ether. The solution was washed with water and dried over sodium sulphate. The ether was removed under vacuum, and the oil obtained (5 g.) purified by chromatography on a column of neutral alumina. The benzene extracts contained the p-aminostyrene (2.2 g.) which was distilled from a small Claisen flask under reduced pressure. The middle fraction

(0.65 g.) was collected and redistilled from a small Claisen flask; b.p. 59°-62°/0.1 mm.; n_D^{24} 1.6220; m.p. 25-26° (Lit: $n_D^{21.5}$ 1.6250[106], n_D^{25} 1.6185[104], m.p. 25°[107]).

p-Methoxystyrene (I, 75-77).

p-Methoxycinnamic acid[101]. - A solution of p-methoxybenzaldehyde (38 g.) and malonic acid (39 g.) in 95% ethanol (80 ml.) and pyridine (8 ml.) was gently refluxed on a steam bath for 7 hrs. The reaction mixture was diluted with hot water and cooled. A first fraction of p-methoxycinnamic acid was filtered off, washed with ice--water (5 ml.), and the combined mother liquor and washings concentrated and extracted with ether. The ether extracts were washed with water and extracted with a saturated solution of sodium carbonate. The aqueous layer was separated, cooled and carefully acidified with concentrated sulphuric acid. The precipitate formed was filtered, combined with the first fraction and recrystallized from aqueous ethanol. The dried p-methoxycinnamic acid (15.5 g.) had m.p. 173° (Lit: 174°).

p-Methoxystyrene. - A mixture of p-methoxycinnamic acid (15.5 g.) hydroquinone (1 g.), copper powder (2 g.) and quinoline[101] (70 ml.) was heated in a distillation flask with a short column, so that the temperature at the top did not rise over 215°. A mixture of p-methoxystyrene and quinoline was collected, taken up in ether (200 ml.), washed with 2N sulphuric acid (3 x 40 ml.) and with water. The neutral ether layer was dried over sodium sulphate, the ether evaporated on a steam bath, and the residue distilled under reduced pressure. The p-methoxystyrene (3.78 g.) had b.p. 96-97/16 mm.; $n_D^{23.5}$ 1.5603 (Lit: n_D^{24} 1.5610[85]).

6.3. Irradiation of vinyl aromatic monomers

6.3.1. ar-Nitrostyrenes (II, 101, 71, 55, 100)

A sample of o-nitrostyrene (659 mg.; m.p. 13-14°) was de-aerated and sealed under vacuum (10^{-2} mm.) in a glass tube. It was irradiated for 72 hrs. at 0° at a dose rate of 0.1 Mrad/hr. and warmed up to 20°. The tube was opened and the liquid added dropwise to petrol (100 ml.). The small amount of precipitate formed was separated by centrifuging, washed with petrol and dried under vacuum. The small amount of solid product isolated

(3 mg. = 0.5%) was not further investigated.

Irradiation of a similarly prepared sample (600 mg.) at 20° for 72 hrs. (dose rate 0.1 Mrad/hr.) gave 2.5 mg. of a slightly yellow powder (0.4%).

A sample of m-nitrostyrene (530 mg.) was de-aerated and sealed under vacuum in a glass tube. It was irradiated at 23° for 72 hrs. at a rate of 0.1 Mrad/hr. The irradiated monomer was added dropwise to petrol (30 ml.). A trace of finely divided precipitate formed was separated by centrifuging, washed with petrol and amounted to about 1 mg. (0.2%). It was not further investigated.

A second sample (run 34; 1.70 g.) was prepared in the same way and irradiated for 18 hrs. at -80° (at a rate of 0.35 Mrad/hr. (total dose 6.3 Mrad). After irradiation, the tube was opened, filled up with petrol (25 ml., saturated with nitrogen) and warmed up to room temperature. The precipitate formed was separated by centrifuging and freeze-dried from dioxane; 8.5 mg. (0.5%) of solid was obtained.

A third sample (run 35; 1.70 g.) was prepared and irradiated as in run (34). After irradiation, the tube was kept at -10° for 125 hrs., warmed up to 20°, opened and the liquid added dropwise to petrol. The precipitate

formed was separated by centrifuging; it was only partly soluble in dioxane, but completely soluble in dimethylformamide. On freeze-drying a dimethylformamide solution, 18 mg. of solid were obtained (1.05%).

Two samples of p-nitrostyrene (m.p. 21°) prepared in the usual way and irradiated for 6½ hrs. at 25° (dose rate 0.1 Mrad/hr.) gave 1.6% and 1.8%, respectively, of gum (runs 108, 111), which was partly soluble in chloroform and dissolved readily in dimethylformamide. Run 110: An equivalent sample was irradiated for 6½ hrs. at 0° (dose rate 0.1 Mrad/hr.) and then warmed up to 25°, the tube opened and the liquid added dropwise to petrol. The precipitate formed was washed with petrol (10 ml.) and dried. Only little solid product (3 mg.; 0.70%) was obtained. Run 109: The irradiation was carried out for 6½ hrs. at -78° at a dose rate of 0.1 Mrad/hr. On adding the sample to petrol, only a trace of precipitate was formed (< 0.5 %). Run 12: A similar sample of p-nitrostyrene (1.07 g.) was irradiated in the solid state for 528 hrs. at 18-20°, (dose rate 0.040 Mrad/hr.); total dose 21.1 Mrad). After irradiation, the original form of the crystals had disappeared. The irradiation product was extracted with hot petrol and dried under

vacuum at 60°. The polymer formed (16.4 %) was soluble in dimethylformamide, but insoluble in benzene, toluene, acetone, and ethyl acetate. A fibre drawn on a glass rod from the polymer melt at 150° showed no crystallinity in an X-ray diagram.

6.3.2. Aminostyrenes (III, 24, 27).

m-Aminostyrene (818 mg.) was irradiated in vacuo for 17 hrs. at 20° at a rate of 0.1 Mrad/hr. The irradiated monomer gave a clear solution in methanol.

p-Aminostyrene (364 mg.; m.p. 23° was irradiated under vacuum at 0° for 18 hrs. (dose rate 0.1 Mrad/hr.). The sample was warmed up to 25° and gave a clear solution in methanol.

6.3.4. p-Vinylbenzoic acid and methyl ester (III, 24, 26)

No polymer was found in a sample of p-vinylbenzoic acid which had been irradiated at 20° for 17 hrs. at a rate of 0.1 Mrad/hr. An equivalent sample, after irradiation at 0°, was warmed on a steam bath and treated with benzene. The solid precipitate was dissolved in sodium hydroxide (2N) and precipitated into hydrochloric acid (2N), filtered and washed with water, methanol (50 ml.) and ether (50 ml.) and dried at room temperature

under vacuum. 257 mg. (36.5 %) of polymer was obtained.

A sample of p-vinylbenzoic acid methyl ester (280 mg.) was irradiated under vacuum for 18 hrs. at 0° at a rate of 0.1 Mrad/hr. The appearance of the crystals had not changed after irradiation; on treatment with methanol, a small amount of polymer was isolated (10-15 mg.; 3.6-5.4 %). Another sample (580 mg.) was given the same dose at 20°; during the irradiation the crystals sintered together. The hard mass obtained was only sparingly soluble in methanol. The product was precipitated from benzene solution into methanol, centrifuged, washed with methanol and dried under vacuum. The polymer (534 mg. = 93%) was obtained as a white powder.

6.3.5. p-Methoxystyrene (III, 25).

Two samples of p-methoxystyrene gave no polymer on irradiation in the solid state (-78°) for 18 hrs. (dose rate 0.1 Mrad/hr.). A sample (550 mg.) irradiated under identical conditions at 20°, gave on treatment with methanol a white polymeric product (40 mg. = 7.4%).

6.3.6. α-Methylstyrene (II, 79-82, 88)

Preparation of samples: Commercial grade α-methylstyrene, obtained from Eastman-Kodak, was distilled under

reduced pressure in a dry nitrogen atmosphere. The first 20% of the distillate was rejected and a middle fraction twice redistilled from sodium.

Run 49: A small amount of the distillation product was redistilled from sodium into a dry pyrex glass tube, frozen in liquid nitrogen, de-aerated and sealed under high vacuum in the usual way. Run 50: Another part of the distilled material was pipetted into a dry irradiation tube, de-aerated and sealed under vacuum. All other samples of α-methylstyrene were made up from monomer which had been twice distilled from sodium in a dry nitrogen atmosphere, de-aerated and sealed.

Unless stated otherwise, the tubes after irradiation were warmed up in tap water at 15° (3-4 min.) and the liquid (15-20 g.) added dropwise to dry methanol (100 ml.). In most cases, an opaque solution was first obtained from which larger particles separated on standing. The suspension was centrifuged, the precipitate washed with methanol (10-20 ml.) and dissolved in a few ml. of chloroform. The solution was transferred to a small weighed tube with a ground-glass joint. The solvent was evaporated at room temperature under vacuum, and the residue dried on a high vacuum line (10^{-3} - 10^{-4} mm.) at room

temperature. Results are given in Table 13.

Table 13. Irradiation of α-methylstyrene

Run	Irrad. time hrs.	Dose rate Mrad/hr.	Total dose Mrad	Polymer found %	Rate % /Mrad
	a) Irradiations at -80°(solid state)				
49	18.5	0.28	5.2	0.029	0.0056
50	18.5	0.28	5.2	-- a)	---
51	16 15	0.28 1.0	19.5	0.068	0.0035
76	17	0.64	10.9	0.12	0.011
52 b)	16 15	0.28 1.0	19.5	0.10	0.005
77 c)	17	0.64	10.9	0.13	0.012
54 d)	16 70	0.28 0.2	18.5	0.135	0.007
	b) Irradiations at 25° (liquid phase)				
53	16 70	0.28 0.2	18.5	3.47 ✱	0.188
55	67	0.18	12.0	0.335	0.0275
79	17	0.64	10.9	15.8	1.45

a) toluene was added to the frozen sample
b) containing 6.6 mol. % benzoquinone
c) containing 6.2 mol. % benzoquinone
d) containing 5.2 mol. % styrene

Lit: α-methylstyrene[77] 0.58 (30°C) 0.01

✱ M.W. found (cryoscop.): 1184.

6.3.7. N,N-Dimethylaminostyrene (m.p. 14°) (II, 93-97, 100-104)

Samples (ca. 1 g.) of N,N-dimethylaminostyrene in glass tubes were de-aerated by the usual freeze-thawing technique and irradiated for different lengths of time and at different temperatures, at a constant dose rate of 0.1 Mrad/hr. Immediately after irradiation, the frozen samples were thawed at room temperature, the tubes broken and the liquid added dropwise to methanol (100 ml.).* The precipitate formed was separated by centrifuging, washed with methanol and dried on a high vacuum line at room temperature. The results obtained are summarised in Table 14.

Analyses of polymers

Run 104b : Found: C, 79.86%; H, 8.62%; N, 9.53%.

Run 120 : Found: C, 80.93%; H, 8.89%; N, 9.84%.

Calculated for $C_{10}H_{13}N$ 81.58%; H, 8.90%; N, 9.52%.

N found in monomer was 9.80%.

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* very viscous products were diluted with an equal volume of chloroform.

Table 14. Irradiation of N,N-Dimethylaminostyrene

Run No.	Dose Mrad	Temperature	Yield %	G (monomer lost)	Remarks
115	0.65	25	3.3	333	low mol. weight (gum)
103	0.65	25	2.85	288	low mol. weight (gum)
121	1.70	25	2.1	81	low mol. weight (gum)
116	0.65	0	4.2	424	
117	0.65	0	3.0	303	sealed with oxygen
104a	0.65	0	13.8	1390	gum
104b	0.65	0	5.7	576	
119	0.65	0	2.7	273	warm ether (3 ml.) added to the frozen sample
118	1.70	0	9.5	370	
122	1.70	0	8.8	340	after irradiation kept for 30 hrs. at 0^{o}.
120	1.70	0	11.6	448	sealed with oxygen
123	1.70	0	6.8	255	sealed with oxygen
100	7.0	0	hard insoluble resin		
104c	0.65	-78	3.5	354	
124	1.70	-180	2.7	101	

Thermal polymerization of vinyl aromatic compounds

Samples (ca. 1 g.) of monomers in glass tubes without initiators were de-aerated, sealed under vacuum and heated in an oven at 107°. After cooling, all liquid products were added dropwise to methanol; all resins were dissolved in a suitable solvent and the polymer precipitated in methanol as usual. The re-precipitation was repeated and the polymer obtained dried under vacuum.

Table 15 Thermal polymerization

	Heating hrs.	Yield %
p-Nitrostyrene	24	85.5 a)
p-Dimethylaminostyrene	24	41.1 b)
p-Vinylbenzoic acid	48	79 c)
- methyl ester	24	67 b)
p-Methoxystyrene	24	54.5 b)

a) soluble in dimethylformamide

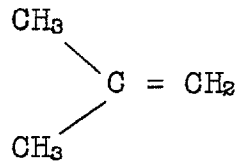
b) soluble in benzene

c) product extracted with benzene; re-precipitated from 2N sodium hydroxide with 2N hydrochloric acid.

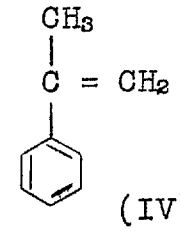
Discussion

α-Methylstyrene

The radiation-induced polymerization of isobutene (III) has been described as an ionic reaction.[58,59,110] It has been stated, that high polymers are formed by irradiation of α-methylstyrene (IV) at low temperatures, although no experimental results have been given.[110]



(III)

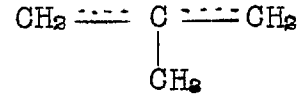


(IV)

A detailed study of the mechanism of the radiation--induced polymerization of isobutene has been given by Collinson et al.[59] Comparing their experimental results with others obtained from experiments on the photo-initiated polymerization of isobutene, using diacetyl as a sensitizer, they concluded, that the active species formed during irradiation (γ-rays or UV) is the resonance stabilized $i\text{-}C_4H_7^{\bullet}$ radical-ion which has structure(V).

/21/ $CH_3COCOCH_3 \rightsquigarrow 2\ CH_3CO^{\bullet}$

/22/ $CH_3CO^{\bullet} + i\text{-}C_4H_8 \longrightarrow CH_3CHO + C_4H_7^{\bullet}$



(V)

The primary act on irradiation is

$$[23] \qquad i\text{-}C_4H_8 \rightsquigarrow R^{\oplus} + e^{\ominus} \quad ,$$

where $R^{\oplus}$ is an ion-radical. Most of the electrons will be captured within 10^{-12} sec. with formation of radicals. This period is far shorter than is necessary for a propagation step in a cationic polymerization, provided the electron capture is not retarded or suppressed.

In the presence of solids, such as ZnO, which are able to absorb electrons, the life-time of the free ions is extended. The enhanced polymerization rate of isobutene in the presence of ZnO was therefore ascribed to electron capture.[58,110] A further contribution towards an extended life-time of ions and free electrons in solids is the reduced collision rate at low temperatures, as has been described[42] in section 3.2.2.

The life-time of growing cationic chains is reduced by the presence of oxygen or benzoquinone.[59] These compounds are competitive electron scavengers; the electron affinity of O_2 is 0.9 eV,[111] that of benzoquinone was estimated[59] as about 0.5 eV. As the ions formed are – at least in the liquid phase – freely mobile, most of the cationic chains will be neutralized

after only a few prcpagation steps.

For α-methylstyrene, which has also the structure $R_1R_2C=CH_2$, one would expect an even higher resonance stabilization of the radicals formed, due to the presence of a conjugated phenyl group. Any radical propagation step with α-methylstyrene would be even slower than in the case of isobutene. Leavitt et al.[112] have attributed the reluctance of α-methylstyrene to polymerize to the difficulty with which the α-methylstyryl radical attacks α-methylstyrene and compared this behaviour with that of allyl acetate.[113] In both cases a degradative chain transfer has been proposed, i.e. growing chains react with monomer without attacking the double bond to form highly stabilized, inactive radicals. However, in co-polymerization the α-methylstyryl radical has a reactivity comparable to that of the styryl radical.[114] Nevertheless, two recent papers[77,115] have described the radiation-induced polymerization of α--methylstyrene as a free radical reaction.

Our results obtained from a limited number of experiments on the liquid phase homo-polymerization of α-methylstyrene, induced by γ-rays, are not compatible with the results of Lowry,[77] who reported a polymerization rate of 0.01 %/Mrad at 30°. Our results are nearer to those

of Hirota et al.[115] who reported a conversion rate of 0.7 - 5% /Mrad. As can be seen from Table 13, the rates found in our experiments are higher than Lowry's result by a factor of 2 - 145. As all our irradiation samples have been prepared in the same way, a difference of this size of order cannot be easily explained. It is noteworthy that Collinson et al.[59] found in the liquid-phase polymerization of isobutene a rather similar scatter of results (factor 30), which they first ascribed to the formation of impurities during sealing, but later explained as due to an uneven distribution of small solid particles which might act as electron traps.

In view of the low reactivity of the α-methylstyryl radical, it would be surprising if trace amounts of impurities were to give such a large difference in the polymer yield. By analogy with isobutene, it seems much more probable, that an ionic mechanism is involved. This seems even more probable in the light of a very recent paper by Bates, Best and Williams.[116] These authors showed that small amounts of water, not removed by more conventional drying techniques, can reduce the maximum G-value obtained (10000) by a factor of 10^3. They pointed out that the role of water as a polymerization inhibitor cannot readily be explained in terms of

radical reactions /24/ and /25/

/24/ $R^{\bullet} + H_2O \longrightarrow RH + OH^{\bullet}$

/25/ $R^{\bullet} + H_2O \longrightarrow ROH + H$

Both these processes are endothermic in the forward direction and the reverse of /24/ is a facile reaction of OH radicals with organic compounds. The authors postulate eq. /26/ for the interaction of water with a propagating cationic centre.

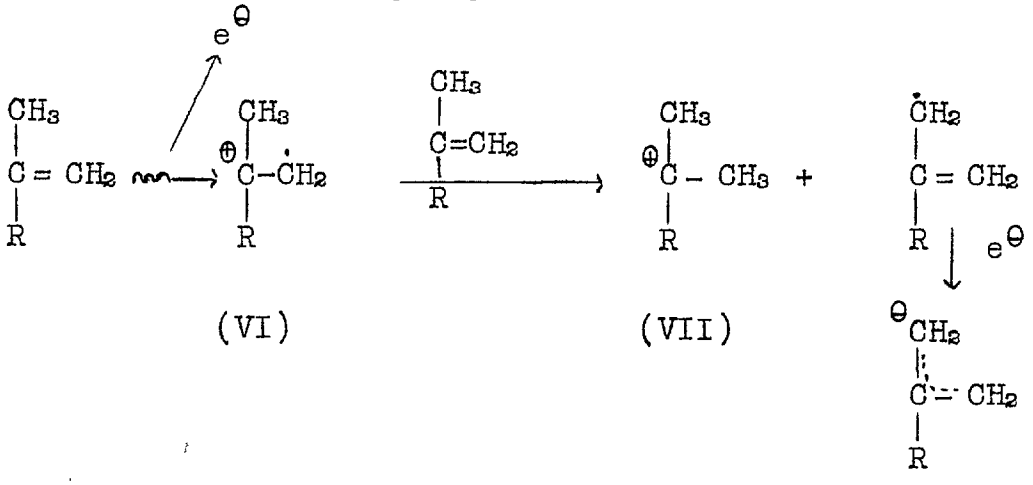
/26/ $$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{C^{\oplus}}} + (H_2O)_n \rightarrow -CH=\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{C}} \quad \text{or} \quad -CH_2-\overset{\overset{CH_2}{\|}}{\underset{\underset{R}{|}}{C}} + H_3O^{\oplus}(H_2O)_{n-1}$$

If the hydronium ion is solvated by surrounding water molecules, reaction /26/ becomes exothermic by virtue of the heat of solution of $H_3O^{\oplus}$. In the presence of water, the equilibrium in eq. /26/ is well on the right-hand side.[117]

Another deactivation mechanism of a cationic centre is the well known exothermic solvolysis reaction

/27/ $$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{C^{\oplus}}} + (H_2O)_n \qquad CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{COH}} + H_3O^{\oplus}(H_2O)_{n-2}$$

Based on these facts, Bates et al. proposed the following mechanism for the radiation-induced polymerization of α-methylstyrene.



(VI) (VII) (VIII)

As the allylic carbanion is stabilized by resonance, the ion pair (VII+VIII) - as it will exist in a surrounding with a low dielectric constant - has a sufficiently long life-time to allow (VII) to undergo many addition (or transfer) steps. In a non-polar medium, water molecules would be rapidly attracted by electrostatic forces to the growing cationic chain ends, where they undergo reaction [26] or [27].

The critical point in this type of radiation-induced reaction is therefore the drying of the monomer. Bates et al.[116] have shown, that even repeated distillation over sodium is not a sufficiently rigorous method for removing traces of water. These authors obtained their

high conversion rates with material which had been dried over activated silicagel and suggested that the effect of adding ZnO[58,59,110] to isobutene may be similar. Bates et al. obtained in this way with α-methylstyrene conversions up to 10%/10^5 rads.

The solid state radiation-induced homopolymerization of α-methylstyrene proceeded at an appreciably lower rate. It is rather doubtful, whether the reaction actually occurs in the solid state. In run (50), toluene was added to the frozen sample immediately after irradiation, and the sample brought up to room temperature in a relatively short time. After removing toluene and part of the monomer at room temperature, no precipitate was formed,* so that one would conclude that the reaction actually occurs in the heterophase system formed during warming up.

Two different groups of compounds have been shown to behave in a similar way:

(a) Acrylamide, methacrylamide etc. (see previous sections)

(b) Styrene[55].

On warming irradiated samples of type (a) compounds, a steady increase in the polymerization rate occurs, heating to the melting point brings about a practically

* only products which were insoluble in methanol have been isolated.

complete conversion within a very short time. This type of temperature dependence is normally ascribed to free radical polymerizations.

Styrene[55] showed practically no reaction at -78° (0.1% /2.1 Mrad), but polymer was formed on warming irradiated samples from -78° to temperatures below the melting point (-30°). The reaction stopped at temperatures immediately above -30°, and for irradiations at room temperature a typical free radical polymerization was observed. By comparison with results from the radiation-induced low temperature polymerization of styrene in different solvents[118], Chapiro and Stannett[55] assigned an anionic mechanism to the corresponding low--temperature heterophase (post-) polymerization.

Sobue and Tabata[56] showed that irradiated acrylonitrile (m.p. -82°) reacts in the solid state in the presence of pyrogallol without any induction period. The solid state reaction had an activation energy of about 0.4 kcal/mol. Whereas between -78° and 0° no reaction occurred, a free radical mechanism occurred at higher temperatures, involving activation energies of 5 kcal/mol. between 0° and 20°, 15 kcal/mol. between 30 and 60°.

The results of our experiments and those of Bates et al.[116] on α-methylstyrene suggest that a different mechanism is involved, as α-methylstyrene seems to polymerize at a higher rate at temperatures between the melting point and 25°. The small amount of polymer obtained (10-50 mg.) did not permit a viscometric determination of molecular weight. These results might have helped to decide, whether the product is formed by a random recombination of neighbouring radicals, such as (VI) and (VIII), or by an ionic post-polymerization. This would mean, that either (VI) has a life-time of at least several minutes and that at the same time electrons are trapped in sufficiently deep "holes" to be released on warming the irradiated monomer, or, reaction (VI) ⟶ (VII) + (VIII) is proceeding even at -80°, but (VII) and (VIII) are efficiently trapped.[x]

Finally, it might be possible that the cationic propagation step in "super-dry" monomer actually takes place in the solid state. Some evidence for this theory has been given in a paper by Andreya and Koton[119], who polymerized a frozen block of α-methylstyrene in the

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[x] see further discussion for the polymerization of p-Dimethylaminostyrene.

presence of gaseous BF_3 at -80°. The rate was considerably higher than at room temperature. It seems surprising that such a result was obtained under conditions which did exclude oxygen and moisture, but hardly to the extent as required by the mechanism proposed by Bates et al.[116] However, it has to be kept in mind, that polymerizations catalysed by BF_3 do not necessarily involve the same initiation steps as the radiation--induced polymerization. It has been rigorously demonstrated by Evans and Meadows[120] that the liquid phase polymerization of isobutene by BF_3 does not take place in absence of traces of water.

p-Dimethylaminostyrene

p-Dimethylaminostyrene (IX) is known to enter into cationic copolymerizations with great ease. The ratios r_i of the propagation rate constants* in the cationic

---

* $M_1^+ + M_1 \xrightarrow{k_{11}} M_1^+$ $\qquad r_1 = \frac{k_{11}}{k_{12}}$

$M_1^+ + M_2 \xrightarrow{k_{12}} M_2^+$ $\qquad r_2 = \frac{k_{22}}{k_{21}}$

$M_2^+ + M_2 \xrightarrow{k_{22}} M_2^+$

$M_2^+ + M_1 \xrightarrow{k_{21}} M_1^+$

where M_1^+ and M_2^+ represent polymer cations having monomers M_1 and M_2, respectively, as their terminal, cation-bearing units. The first subscript attached to the propagation rate constant refers to the reacting cation, and the second to the monomer.

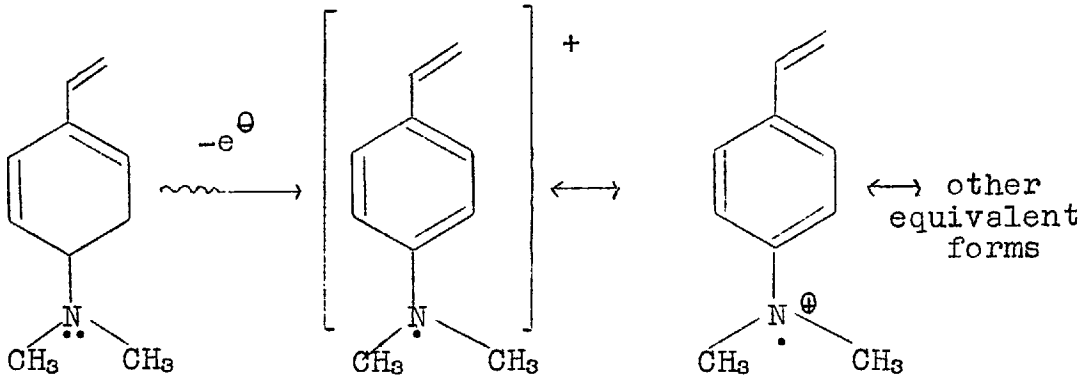
copolymerization of α-methylstyrene (M_1) and p-dimethylaminostyrene (M_2) are: $r_1 = 0.035$ and $r_2 = 31\ (\pm 19)$.[121] Pepper[122] calculated the order and approximate magnitude of reactivity of several vinylic monomers towards carbonium ions. The values for a small number of these compounds are given in Table 16.

Table 16

p-Dimethylaminostyrene	190
p-Methoxystyrene	20 - 100
α-Methylstyrene	7
Styrene	1

No account of a cationic homopolymerization of (IX) could be found in the literature.

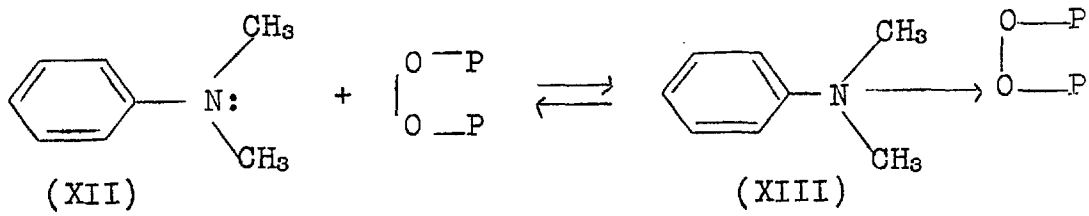
On irradiating (IX) with γ-rays, one obtains an ion-radical with the general formula (X)



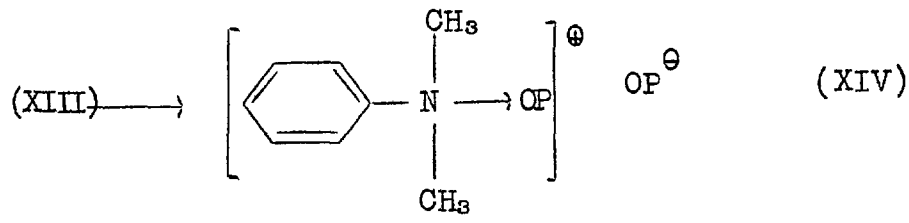
(IX) (X) (XI)

It seems unlikely that (XI) can initiate a free radical polymerization, as Bartlett and Nozaki[123] were unable to initiate the polymerization of styrene with tritolylaminium perchlorate ($(C_7H_7)_3\overset{\oplus}{N}\cdot\ ClO_4^{\ominus}$). This would be in agreement with our experimental results (Table 14), which show that the polymerization of (IX) proceeds at a higher rate at low temperatures than at room temperature.

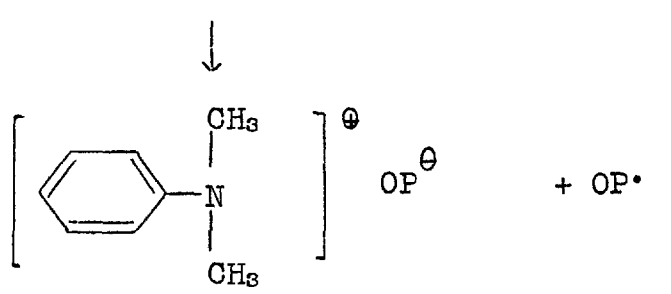
An aminium radical similar to (XI) has been postulated as an intermediate product in the polymerization of vinyl compounds in the presence of amines and benzoyl peroxide.[124-126]



(XII) (XIII)

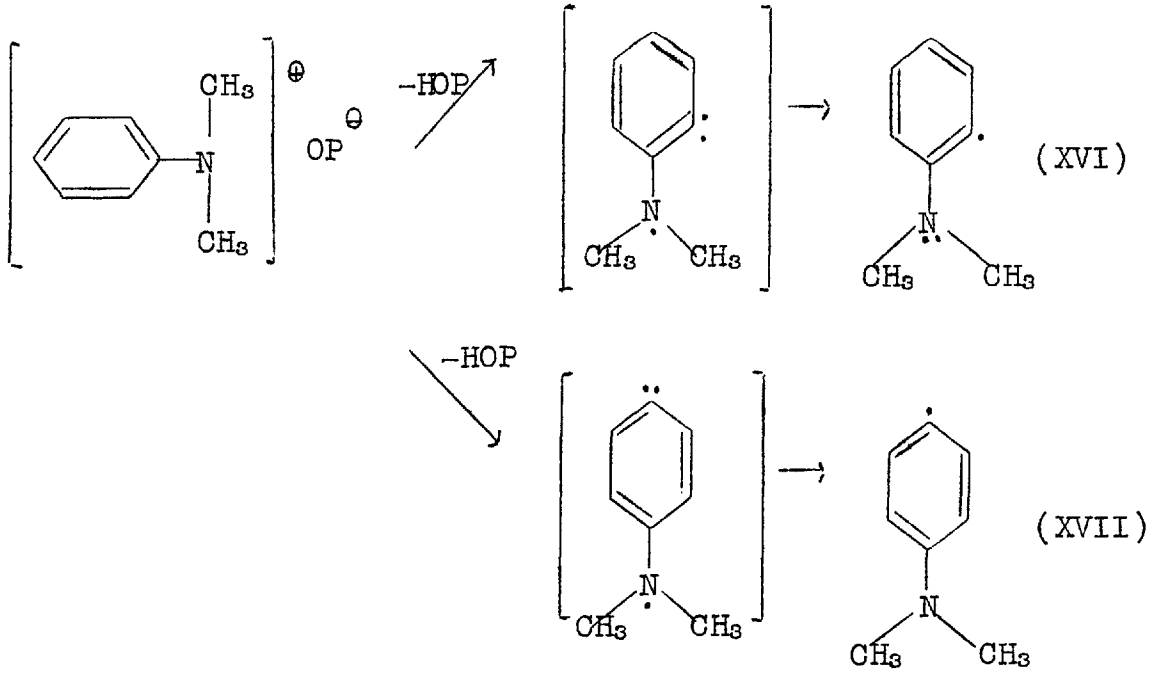


(XIV)



(XV)

The aminium radical cation (XV) is stabilized by loss of a proton to give finally radicals of the type (XVI) or (XVII), which may initiate radical chains.[124]



Excluding, for the reasons given, a free radical polymerization, it seems possible that in the solid state polymerization some freely mobile protons add to a vinyl bond and initiate a cationic chain. The inhibition effect of amines in cationic polymerizations which has been reported by George, Wechsler and Mark[127] need not necessarily apply in solid state reactions.

Experiments 104c, 119, 122 and 124 (Table 14) suggest, that the reaction really occurs in the solid state, and not during melting after irradiation. It

is difficult to imagine that cations have a life-time of over 30 hrs. in a solid state system at 0^{o} (run 122).

The monomer used in our experiments was not specially dried; the solvation of protons is therefore - at least for temperatures above 0^{o} - a possibility (eq. 26, 27). However, the situation is somewhat different from that in the α-methylstyrene system. The reaction proceeds faster in the solid state than in the liquid state. Also, p-dimethylaminostyrene is a more polar molecule than α--methylstyrene, which may be of some relevance.

Hydrogen acids give on interaction with alkenes mainly dimers or cyclic products, but in a few instances high polymers have been obtained. Examples are the low temperature polymerization of α-methylstyrene in methylene chloride by concentrated sulphuric acid,[128] and the formation of polystyrene under similar conditions, catalized by hydrobromic acid. It was noted in both cases that water had a retarding influence.

Finally, we would like to add, that the infra red spectrum of thermally polymerized p-dimethylaminostyrene was identical with the spectrum of the γ-irradiation polymer.

p-Vinylbenzoic acid

No definite conclusions regarding the mechanism can be made from the few data obtained. The monomer polymerized without catalyst at 100° in the solid state, but did not form any polymer on irradiation at 20° or 0°. On warming the irradiated sample for 2 hrs. at 100°, polymeric product was formed. Only an exact comparison of the conversion rates and molecular weights would show whether the irradiated monomer reacts at 100° at a higher rate than the non irradiated monomer.

p-Vinylbenzoic acid methyl ester

The solid state polymerization of this monomer has features similar to those found in acrylamide and methacrylamide. At temperatures well below the melting point, the reaction rate is low; it increases considerably at higher temperatures. It is known that hydroquinone acts as an inhibitor in the spontaneous polymerization of this monomer in solutions, and that therefore a free radical mechanism seems to be involved. In view of the temperature dependency of the γ-ray polymerization, in this case also a free radical mechanism seems to be involved.

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Appendix I

Infrared and Ultraviolet Data

Introduction

Infrared spectra of N-aryl substituted methacrylamides have not yet been fully described in the literature. Sokolova and Nikitin[1] reported recently the infrared bands of some of these compounds, in the solid state and in solution, between 3500 $cm.^{-1}$ and 3200 $cm.^{-1}$ (table VII). Some useful information is available in papers by Richards and Thompson,[2] Gierer,[3] Davison and Bates[4] and in the book of Bellamy,[5] which gives further references to original papers. The assignment of phenyl bands (tables IV, V) is based on a paper by Randle and Whiffen.[6]

We present data from infrared spectra of methacrylamide, fifteen N-substituted methacrylamides and some of the corresponding polymers.

Experimental

The infrared spectra were determined with a Grubb--Parsons D.B. 1/S.4 spectrometer using NaCl optics at $25^{o}C(\pm 1)$. ANALAR chloroform and ANALAR carbon tetrachloride were used as solvents. Discs have been prepared with potassium bromide and potassium chloride.

The preparation and properties of the compounds investigated have been described in the main part of this thesis.

Results

All absorption maxima are given in wave numbers. Phenyl bands of monomers are presented in tables IV and V, all other monomer bands in tables I - III. In most cases a range between 3500 $cm.^{-1}$ and 800 $cm.^{-1}$ is covered, but for ortho substituted methacryl anilides values down to 700 $cm.^{-1}$ are included. Absorption bands from spectra of polymers are given in table VI.

Abbreviations (tables I - VII)

The names of the compounds are given in the tables under the heading "Mark" as follows:

$-NH_2$	methacrylamide
$-NH-\phi$	methacrylanilide
$-\overset{CH_3}{\underset{}{N}}-\phi$	methacryl-(N-methyl)anilide
o-, m-, p-CH_3	methacroyl-(N-o-, m-, p-)toluidide
o-, m-, p-Cl	N-(o-, m-, p-chlorophenyl)methacryl-amide

o-, m-, p-OC_2H_5	N-(o-, m-, p-ethoxyphenyl)methacrylamide
o-OCH_3	N-(o-methoxyphenyl)methacrylamide
o-Br	N-(o-bromophenyl)methacrylamide
α-napht	N-(α-naphtyl)methacrylamide
β-napht	N-(β-naphtyl)methacrylamide

"State: $CHCl_3$, CCl_4" indicates that a solution in chloroform or carbon tetrachloride was employed.

"State: KBr, KCl" indicates that the solid was examined in a halide disc.

Band intensities (relative intensities within one particular spectrum)

w weak m medium s strong vs very strong

Table VII

NH - Absorption (Sokolova, Nikitin[1])

	Solid State NH (bound)	NH (free)	In CCl_4 Solution NH (bound)	NH (free)
p-OCH_3	3300	---	3344	3436
m-OCH_3	3313	---	3356	3436
o-OCH_3	3344	3425	3349	3425
p-OC_2H_5	3306	---	3359	3442
m-OC_2H_5	3300	---	3359	3442
o-OC_2H_5		3418	3351	3431

Table I Monomers

Mark	State	νN – H free	νN – H bonded	A	Amide I	νC = C	Amide II
–NH_2	$CHCl_3$	3422m	3343m	2938w	1672vs	1626s	1575s
	KCl	3300m		3123m 2734w	1693s	a)	1597s
–NH–ø	$CHCl_3$	3422w	3330w	3056w 2997w	1667s	1618s	1510m
	KCl	3277m		3056w	1661s	1621s	1530s
CH_3 –N–ø	CCl_4			3117w 3075w 2956w	1667s	1639s	1509s
	KBr			3075w 2938w	a)	a)	1497m
o–CH_3	CCl_4	3480w	3360w	3100w 3000w 3056w 2957w	1698s	1637s	1515s
	KCl		3385w 3246s	3123w 2965w 3047w 2938w	1664s	1629s	1520s
o–OCH_3	$CHCl_3$	3400w		2944w a)	1672s	1626m	1516s
o–Br	$CHCl_3$	3385w		a)	1684m	1629m	1508s
	KCl	3203w b)		2938s b)	1681m 1653m	1618s	1512vs

Table I (cont.)

Mark	State	B	C	D	δ=C-H out of plane	Other Bands
$-NH_2$	$CHCl_3$	1450m 1400m 1365m			947m 923m	1086w
	KCl	1450m 1405m 1384m 1369m			956w 932m	1232m 1106m 1012m 825m 781m
$-NH-\phi$	$CHCl_3$	1454m 1429m 1371w			947w 926m	1331m 1282m
	KCl	1372w	1333m 1321m		937m 921w	1290m 921m 893m
CH_3 $-N-\phi$	CCl_4	1465m 1426m 1375m	1312m		948w 919m	1124s 1115s
	KBr	1455m 1427m 1379m	1307m		929m 906m	1294w 881w
o-CH_3	CCl_4	1458s 1415w 1377m	1313s	1250m 1188w	947m 919s	1291m 1049w 963w
	KCl	1454s 1442s 1380m	1309m 1329w	1248w 1177w	937m 913m	1279w 1201w 1017w 963w 853w
o-OCH_3	$CHCl_3$	1457s 1432m 1374w	1287m	1242w	944w 923w	1334m 1170w 956w 898w
o-Br	$CHCl_3$	1432m 1375w	1307s 1292m		945w 923w	1023m
	KCl	1461w 1430s 1370w			932w 911w	1048w

Table II Monomers

Mark	State	ν_{N-H} free	ν_{N-H} bonded	A	Amide I	$\nu_{C=C}$	Amide II
α-napt	$CHCl_3$	3423w		a)	1691s	1629m	1517 m
o-Cl	CCl_4	3423m		3094w 2941w 2992w	1701s	1637m	1509s
	KBr	3423w	3213s	a)	1664s	1629s	1516s
o-OC_2H_5	CCl_4	3454w		3105w 2963w 3054w	1700s	1664m	1523s
	KCl	3423m		3055w 2938w 2982w	1684s	1631m	1528s
p-CH_3	CCl_4	3440w	3304w	3033w 2935w 2980w	1689s	1634s	1508s
	KBr	3255m		a)	1664s	1626s	1525s
p-Cl	$CHCl_3$	3403w	3331w	3075w 2956w	1680vs	1626m	a)
	KCl	3266w		a)	1658s	1621s	1526s
p-OC_2H_5	$CHCl_3$	3423m	3330w	2973m 2933m	1675s	1626s	1517s
	KCl	3320w		2973w 2930w	1661m	1621m	1523vs

Table II (cont.)

Mark	State	B	C	D	δ=C - H out of plane	Other Bands
α-napt	$CHCl_3$	1459s 1397m 1375w		1177w	948w 923m	1580w 1154m 852w 1347 1263 852
o-Cl	CCl_4	1457m 1439s 1379w	1313s	1236m	945m 923s	1152s 1108s 953w 893w
	KBr	1436s 1375w	1325m	1247m 1177m	936m 914m	1064m 976w 964w 846w
o-OC_2H_5	CCl_4	1459s 1395w 1374w	1296m	1250s 1170m	945w 921m	1341m 1209m 1092m 1050w 959w 931w 831m 899w
	KCl	1455s 1394m 1376w	1289m	1250s 1170m	 927m	1730w 1340m 1209m 1045s 958w 898w
p-CH_3	CCl_4	1456s 1407s 1384m	1321s	1245s	944w 921m	1341w 1216m 1155s 1045w 891w
	KBr	1451m 1374w	1322m 1304w	1250m	934m 916m	1332m 1111w 850w 834w 800w
p-Cl	$CHCl_3$	1458w 1398m	1309m	1154w	945w 923w	1090m 832s
	KCl	1448m 1372m 1395s		1170w	932w 925w	1089w 1047w 899w
p-OC_2H_5	$CHCl_3$	1450m 1411s 1394m 1377m	1320m 1303m	1242s 1163s	941w 924m	1089w 1047m 899w
	KCl	1454w 1413w 1396w	1287w	1252s	925m	1334w 1050m 903m 814w

Table III. Monomers.

Mark	State	ν N – H free	ν N – H bonded	A	Amide I	ν C = C	Amide II
m–CH_3	CCl_4	3423m	3348w	3028w 2953w 2913w 2868m	1686s	1626s	1515s
	KCl	3300s		a)	1661s	1626s	1527s
m–Cl	$CHCl_3$	3392w		a)	1678s	1626s	1503s
	KCl	3234w		a)	1664s	1625s	1536s
m–OC_2H_5	$CHCl_3$	3443m	3368w	3094w 3010w 2964w	1689s	1639m	1508m
	KCl	3309s		3125w 3077w 2962m 2921w 2877w	1661s	1623m	1530s
β–napht	$CHCl_3$	3403w		a)	1675s	1629s	1522s

Table III (cont.)

Mark	State	B	C	D	δ = C – H out of plane	Other Bands
m–CH_3	CCl_4	1450m 1432s 1375m	1310m	1259w 1183s	941m 919s	1302m 1142m 895m
	KCl	1451m 1433s 1376w	1325m 1290m	1263m 1158s	931m 925m	1149w 906w 874w 800vs
m–Cl	$CHCl_3$	1450w 1404s 1377w	1306s	1157s	946w 920m	1100m 855w
	KCl	1446w 1421s 1375w	1319w	1250m 1171w	941m 921w	1263m 1092w 865s 829w 800m
m–OC_2H_5	$CHCl_3$	1440s 1393m	1312m 1284s	1181m 1167m	948m 923m	1116m 987w
	KCl	1446s 1392m	1318w 1304m	1160s	945w 923w	1479m 1271s 1212s 1112m 1014m 998w 852s 824w 804m
β–napht	$CHCl_3$	1450w 1427m 1388w 1370s	1276w	1181w 1148m	949w 921w	1121w 1045w 966w 890w 852w

Table IV Phenyl bands of monomers.

		C-C Stretching Vibrations		In-plane C-H Deformation				Ring Breathing	Other Phenyl Bands
Lit.[6]		1506±7	1499±7 1588±9	1240±8	1156±5	1177±6	1072±7	1001±4	
Mark	State								
-NH-ø	$CHCl_3$	1595s	1476w	1250w	1160w		1079w	1009m	
	KCl	1600s	1494m	1245m		1170w	1080w	1010w	
CH_3	CCl_4	1603s	a)	1238m	1160w		1080w	1009w	
-N-ø	KBr	1595s	1497s	1242m		1177w	1075w	1002w	
Lit.		1609±10 1575±9	1490±11	1159±7	1126±12	1031±5			
o-CH_3	CCl_4	1595m	1493s	1156s	1114w	1036w		1005w	
	KCl	1608m	1493s		1120w			1004w	853w 804m 762w 748s 714w
o-OCH_3	$CHCl_3$	1600s	1479m	1156m	1115m	1027m		1009w	895w 796w 771w 750s 690w
o-Cl	CCl_4	1595s	1473m	1163s	1131m	1036s		1007w	
	KBr	1597s 1582s	1482	1153w	1129w	1036m		1007w	846w 856w 798m 750s 690w
o-Br	$CHCl_3$	1590s	1461w	1159m	1121w			1007w	
	KCl	1573m	1468s						853w 841w 797w 748s
o-OC_2H_5	$CHCl_3$	1605s	1488m	1160m	1122s			1010w	
	KCl	1605s	1488m	1160m	1120s			1008w	898w 799w 791w 750s 700w

Table V Phenyl bands of monomers

		C-C Stretching Vibrations		In-plane C-H Deformation				Out-of-plane C-H Deformation	
Lit.[6]		1620±8 1571±11	1512±12		1179±7	1125±10	1018±10	961±12	817±13
Mark	State								
p-CH_3	CCl_4	1602s	1508s	1291w	1183m	1121m	1019m	959w	824w
	KBr	1603s	1525s	1289w	1174m	1123m	1022w	958w	817w
p-Cl	$CHCl_3$	1592m	a)	1285w			1020w		817s
	KCl	1597s	1526s		1182m		1015m		823s
p-OC_2H_5	$CHCl_3$	1600s	1517s	1287m		1117m	1010w	957w	831s
	KCl	1603m	1523vs	1285w	1170m	1120m	1016w	966w	833s
Lit.[6]		1611±9 1590±7	1499±7		1165±6	1081±10	1045±7	965±10	875±10
m-CH_3	CCl_4	1613s 1592s	1488s		1166m	1091w	1039w	956w	895s ?
	KCl	1613s 1592m	1490s		1170w			963w	890s ?
m-Cl	$CHCl_3$	1592s	1479s		1157s	1077w			880m
	KCl	1592s	1492s			1079w		960w	877m
m-OC_2H_5	$CHCl_3$	1608s	1488s		1157w	1089w	1043w	987w	907w
	KCl	1605s	1492s			1079w		987m	907w

Table VI. Polymers (in KCl discs)

Mark	ν N – H	A	Amide I	Phenyl	Amide II	Phenyl	B	
$-NH_2$	3320m	3172w 2938w	1668s		1608m			1461w 1390w
o–CH_3	3387w	3165w 2891w	1678s	1587s	1515s	1483s	1448s	1380w
o–OCH_3	3354s	2890w 2840w	1675s	1600s	1523vs	1483m	1461s	1389w
o–Cl	3336s	2891w	1684s	1592s	1515vs		1434s	1385m
o–Br	3360m	2929w	1684s	1584s	1513vs	1471m	1432s	1384w
o–OC_2H_5	3355m	2902w	1675s	1600s	1523vs	1483s	1446s	1390w
α–napht	3331s	2902w	1675s	1595w	1523s	1488s	1440w	1398m
p–CH_3	3345m	2913m	1675s	1595w	1509vs	a)	1461m	1400s
p–Cl	3224m	2916w	1672s	1592s	1517vs	1492w		1396s
p–OC_2H_5	3350w	2965w 2910w	1672m	1600w	1509vs	1478w		1394w
m–Cl	3340s	2913w	1678s	1592s	1517vs	1479s	1419m	
m–OC_2H_5	3385m	2991m	1689m	1613s	1534vs	1501s	1444s	1398w

Table VI (contd.)

Mark	C	Phenyl Bands				Other Bands
$-NH_2$						1202w 1118w 873w
o-CH_3	1301m	1156m?	756s			1250m 1186w 1048w
o-OCH_3	1286w	1155w	1028m	749vs		1429m 1250s 1217w 1174w 1114w 1046w
o-Cl	1298s	1153m	1031m	941w	752vs	1235w 1053w 900w
o-Br	1296s	1154m	1026s	940w	752vs	1233w 1047w 905w
o-OC_2H_5	1290m	1158w	1044s	930w	748s	1331 1209 1250s
α-napht		1183m	1017w			1340m 1253m 1153m 1115m 792s 769s
p-CH_3	1308s			873w	810s	1238m 1149w 1118m 1080w 1045w
p-Cl	1303s		1014m	827vs		1239s 1155m 1091m
p-OC_2H_5	1301w		1047m	824vs		1409w 1230s 1116w 923w 900w
m-Cl	1296m	1077w	918w	884m	782vs	1269m 1242w 1156m 1100w
m-OC_2H_5	1266m 1138w	1164m	1050s	882w	774s	1266w 1196s 1118w

Discussion

1. Spectra of monomers (tables I - VI)

3500 - 2900 cm.$^{-1}$ region

Infrared spectra of anilides are rather complicated in this region, which contains NH bands, CH stretching bands of the ethylenic double bond and of phenyl groups, followed by the CH stretching region of CH_3- and CH_2--groups. As might be expected, the resolution of the NaCl prism is not sufficient to give all the details.

We have been particularly interested in the NH stretching vibrations. In general, the solution spectra of N-substituted methacrylamides show two NH bands at ca. 3450 cm.$^{-1}$ and 3330 cm.$^{-1}$; the first one may be assigned to free NH groups, the second one to bonded NH groups[1] (table VII). Some ortho substituted methacryl anilides show free NH- groups even in the solid state, whereas all meta and para isomers have only bonded NH- groups.

Amide I and Amide II Bands

In solution, the amide I band of methacrylamide is at 1672 cm.$^{-1}$, and the corresponding band in methacryl-anilide occurs at a slightly lower frequency (1667 cm.$^{-1}$).

The shift is in the opposite direction to that found[3] for acetamide (1679 $cm.^{-1}$) compared with acetanilide (1688 $cm.^{-1}$).

Due to change in solvent, no definite conclusion can be drawn from the relative positions of differently substituted anilides. It may be added that Gierer[3] found that substitution in the phenyl group has no effect on the carbonyl absorption frequency.

In the solid state, methacrylamide absorbs at 1693 $cm.^{-1}$, i.e. 21 $cm.^{-1}$ higher than in solution. For methacrylanilide, the difference between solution and solid spectrum in the amide I region is very small. All substituted methacrylanilides absorb in the solid state at lower frequencies than in solution.

Gordy[7] and Richards and Thompson[2] found that in the solid state the stretching frequency of the carbonyl group in unsubstituted or N-monosubstituted amides lies at a much lower value than in dilute solution in dioxane, whilst the amide II band in the solid state lies at higher frequencies. They concluded from their experiments that the frequency of the carbonyl group is reduced by hydrogen bonding. Following this theory, one would expect only a small shift for N-(o-ethoxyphenyl)- and N-(o-bromophenyl)-methacrylamide which

show free NH in the solid state in the 3400 cm.$^{-1}$ region. In the case of the o-ethoxyphenyl compound, the carbonyl frequency shifts only by 16 cm.$^{-1}$, compared with, e.g. 34 cm.$^{-1}$ in the case of the methacroyl--o-toluidide. In N-(o-bromophenyl)methacrylamide the amide I band is split into a doublet, as has been found previously in some concentrated amide solutions;[2] it seems, therefore, that this splitting may not be due to Fermi-resonance, such as occurs in cyclopentanone. The result of the o-chlorophenyl compound is in no way different from that of most other substituted anilides, but Sokolova et al.[10] have shown in measurements at different temperatures, that the hydrogen bonding in this compound is weak, and the polymerizability similar to that of the o-bromophenyl- and o-ethoxyphenyl compound.

In all the anilides investigated, the amide II band appeared at higher frequencies and with relatively higher intensity in the solid state than in solution.

C = C Stretching Band near 1600 cm.$^{-1}$

The band appears with a rather high intensity in all our monomer spectra (solid and solution) around 1629 cm.$^{-1}$ The deviations from this value seem to be of

random character; N-(o-ethoxyphenyl)methacrylamide in carbon tetrachloride has a singularly high value (1664 cm.$^{-1}$).

1480 - 1000 cm.$^{-1}$ Region

A large number of C - H deformation bands are found in this region, where bands near 1375 cm.$^{-1}$ and 1450 cm.$^{-1}$ have been assigned to the methyl group.[8] Other bands belong to the in-plane C - H deformation of the aromatic nucleus and to skeletal deformations. We have grouped corresponding wave numbers in the tables -.

Out-of-plane =C - H deformations near 930 cm.$^{-1}$

The out-of-plane C - H deformations in compounds of the type $R_1R_2C{=}CH_2$ occur at 890 cm.$^{-1}$ Carbonyl groups adjacent to the double bond raise the frequency to 930 - 945 cm.$^{-1}$ Davison and Bates[4] give some results for this type of compounds (in CCl_4):

	δ CH cm.$^{-1}$
$CH_2{=}C(CH_3)COOH$	947
$CH_2{=}C(CH_3)COOR$	939 $\pm$ 1
$CH_2{=}C(CH_3)COR$	930 $\pm$ 1

In the infrared spectra of substituted methacrylanilides, we observed two rather weak bands in this region; the first one was near 945 cm.$^{-1}$ in solution (932 cm.$^{-1}$ in the solid state) and the second near 922 cm.$^{-1}$ in solution and from 913 to 923 cm.$^{-1}$ in the solid state. As only one band would be expected for this type of compound, we assume that accidental aplitting (Fermi-resonance) of the 930 cm.$^{-1}$ band has occurred. The arithmetical average of the two frequencies concerned (solution) has a constant value of 934±2 cm.$^{-1}$, very near the value of 930 cm.$^{-1}$ suggested by Davison and Bates for this type of structure. This constant value would suggest that the vinyl bond is not conjugated with the aromatic system <u>via</u> the amide link, as one would then expect to find frequency shifts due to the substituents on the benzene ring. This result is in contradiction to the findings of Petrova, Sokolova et al.[1,9,10] from polymerization and copolymerization experiments.

<u>Phenyl Bands</u>

All bands identified as phenyl are shown in the columns of tables IV and V, headed by the values reported by Randle and Whiffen.[6]

2. Spectra of Polymers

On the whole the polymer spectra are less well resolved. In the N-H stretching region, only one band near 3360 $cm.^{-1}$ is shown. The amide I and amide II absorptions of the different polymers have rather constant values around 1675 $cm.^{-1}$ and 1515 - 1520 $cm.^{-1}$ The 1440 $cm.^{-1}$ band is rather strong which might be due to superposition of a phenyl and a CH_3 band. As one would expect, the monomeric $\nu C=C$ band near 1630 $cm.^{-1}$ and the =C-H bands between 950 $cm.^{-1}$ and 900 $cm.^{-1}$ have disappeared in the polymer spectra.

3. Literature

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Infrared Spectra of Styrenes

It was found, that the absorption bands in corresponding monomers and polymers have practically identical positions; the values given in Table VIII have been obtained from spectra of monomers. The positions of the C=C stretching band and of the two vinyl bands were identified by a comparison of the spectra of corresponding monomer and polymer and are underlined in Table VIII.

Ultra-violet Spectra of Styrenes

All ultra-violet spectra were obtained with a SPECTRACORD spectrophotometer. Solvents used, absorption maxima (mμ) and molecular extinction coefficients (ε) are given in Table IX.

Table VIII. Infrared Spectra of Styrenes (1550-820 $cm.^{-1}$)

Substituent	Bands ($cm.^{-1}$)
p-OCH_3	1629?m, 1605m, 1575w, 1511s, 1462m, 1408w, 1321w, 1300m, 1250s, 1175s, 1116m, 1040m, 1024m, 990m, 900m, 833s, 816w.
p-$COOH$[a]	1745w, 1701s, 1613m, 1422s, 1319m, 1290s, 1220w, 1186m, 1131w, 1115w, 1083w, 1018w, 988m, 920m, 863m.
p-$COOCH_3$	1723s, 1628?w, 1607m, 1567w, 1508w, 1438m, 1404m, 1312m, 1279s, 1180m, 1110s, 1018m, 990w, 976w, 917w, 860m, 833w.
p-$N(CH_3)_2$	1608s, 1516s, 1477m, 1440m, 1405w, 1352s, 1326m, 1220m, 1186m, 1163s, 1129m, 1062m, 992m, 948s, 887m, 821s.
p-NH_2	1616s, 1510s, 1432w, 1409w, 1341w, 1279m, 1206v, 1174m, 1129w, 991m, 894m, 833s.
m-NH_2	1617s, 1602s, 1581s, 1496m, 1461m, 1413w, 1318w, 1297m, 1270w, 1160m, 993s, 910s, 867s.

Table VIII (contd.)

Substituent	Bands ($cm.^{-1}$)
o-NO_2	1609m, 1571s, 1522s, 1482m, 1446m, 1413m, 1348s, 1302s, 1278w, 1200m, 1163w, 1144w, 1080w, 1060w, 1024w, 984m, 928s, 858s.
m-NO_2 [a]	1634w, 1523m, 1486w, 1440w, 1409v, 1349vs, 1312m, 1097w, 1084w, 997m, 920s, 902m.
p-NO_2 [a]	1597m, 1512s, 1345s, 1179w, 1112w, 1012w, 987w, 922m, 858s.

[a] solution in CCl_4

Table IX. Ultra-violet spectra of styrenes

	in ethanol		in dimethylformamide	
Substituent	λ (mμ)	ε	λ (mμ)	E_1^1
p-OCH_3	259 M	18950		
	292 M	2440		
	303 M	1370		
p-COOH	213 M	10780		
	266 M	22200		
	295 I	1020		
p-$COOCH_3$	214 M	8560		
	269 M	23400		
	295 I	1020		
p-$N(CH_3)_2$	222 M	9550		
	295 M	20600	297 M	1000
Dimer	260 I	15000		
	295 M	25400		
Polymer			263 M	227
			303 M	58.3

Table IX (contd.)

	in ethanol		in dimethylformamide	
Substituent	λ (mμ)	ε	λ (mμ)	E_1^1
m-NH_2	228 M	25200		
	250 I	10420		
	313 M	1153		
o-NO_2	232 M	15200		
	257 I	7450		
	305 I	2360		
m-NO_2	240 M	29200		
	273 I	6100		
	315 I	1340		
p-NO_2	220 M	9700	305 M	915
	300 M	18000	312 M	930
Polymer			280 M	540

E_1^1 is the absorption of 1 cm. pathlength of a 1% solution.

M and I stand for absorption maximum and inflection, respectively.

Appendix II

D o s i m e t r y

(γ - Rays)

1. Introduction

An accurate determination of the amount of chemical change produced in a suitable dosimeter solution as a function of the γ-ray energy absorbed affords a simple and rapid method for determining the dose received by other solutions. As no exact information is available for the energy absorptions in solids, the results of calibration of radiation fields with solutions are also used for dose calculations in solids, taking into account differences in electron densities. For most organic compounds, containing only light elements, this difference is negligible.

The dosimeters proposed are based on quite different chemical reactions: discoloration of dyestuffs, polymer formation, phenol formation from benzene in water, oxidation of ferrous ions, reduction of ceric ions. Most workers use the radiation-induced oxidation of ferrous salt solutions in aqueous sulphuric acid, introduced by Fricke.[1,2]

Calibrations of ferrous sulphate dosimeters have been carried out by comparing the ionization current observed in an air-filled ionization chamber and the

chemical change produced in a solution contained in a similar chamber placed in the same radiation field. The energy absorbed in the condensed system is derived from the measured ionization in air.

Whereas early calibrations gave G-values ($G_{Fe^{3+}}$ = number of Fe^{3+}-ions formed/100 eV) between 15 and 22, more recent work comparing ionisation method[3,4] and colorimetric measurements[4,5] agree within narrow limits on a G-value of 15.5.[3]

The G-value of the reaction is independent of the initial Fe^{2+}-concentration in the range between 0.6 mM and 10 mM, provided enough oxygen is present.[6,14] The oxidation of Fe^{2+}-ions is linearly proportional to the absorbed dose[2,7] for all dose rates between 6 and 2.10^5 rad/min.[6,8] $G_{Fe^{3+}}$ is constant for sulphuric acid concentrations between 0.1 N and 0.8 N.[9] The thermal coefficient of the oxidation can be neglected for irradiation temperatures between 20° and 30°C.[13,15]

The ferric ions formed can be determined spectrophotometrically at 304 mμ; the extinction coefficient of ferric ions in 0.1 N sulphuric acid has been found to be 2115 (±20) at 20°C, decreasing by 0.7%/°C between 20° and 30°.[3,10,11] Analytical grade ferrous salts ($FeSO_4.7\ H_2O$ or $Fe_2(NH_4)_2(SO_4)_2.6\ H_2O$) and

concentrated sulphuric acid may be used without further purification.[3] Special care has, however, to be taken for the preparation of distilled water and for the cleaning of all vessels involved.[3] Addition of sodium chloride (analytical grade) up to concentrations of 10^{-3}M suppresses the influence of traces of organic impurities.[7,12]

2. Experimental (II, 2)

a) Calculation of dose

Absorbed dose measurements are made by irradiating a solution of 10^{-3}M $Fe_2(NH_4)_2(SO_4)_2$ and 10^{-3}M NaCl in 0.1 N H_2SO_4 and measuring the optical density at 304 mμ after irradiation. Taking an extinction coefficient of 2115 ± 20 (20°C) for ferric ion and a $G_{Fe^{3+}}$-value of 15.5, we obtain:

$$\text{Dose} = 2.94 \times 10^4 (1 - 0.007\ t).E \text{ rad}$$
$$= 1.84 \times 10^{18} (1 - 0.007\ t).E \text{ eV/g}$$

where E = optical density at 20°C

T = sample temperature in °C

t = T°C - 20°C

In connection with the interaction of ^{60}Co-γ-rays with organic compounds, containing only light atoms, the

Compton-effect is predominant (> 99%). The contribution of the Compton-effect to the mass absorption coefficient, μ/ϱ, depends solely on the number of electrons per gram of the absorber. For all the lighter elements, this is very nearly 3.10^{23}, being markedly greater only for hydrogen, for which it is about $6.10.^{23}$ Thus, for air, water and nearly all organic compounds, the relative contribution of the Compton-effect is about the same, regardless of the atomic composition.

b) Calculation of G-values in polymerization reactions.

$$G_{\text{(for monomer lost)}} = \frac{\text{number of monomer molecules removed}}{100 \text{ eV}}$$

for 1 g: 1 g monomer absorbed n [eV]

polymer found m [g]

$\therefore$ x monomer molecules lost

c) Radioactive decay of ^{60}Co.

^{60}Co decays with a half life of 5.3 years. For a given sample position relative to the source we got a dose rate

$$D_t = D_o . e^{\pm 0.1302\ t}$$

(Fig 1)

where D_t = dose rate before/after 1.5.1960 (date of calibration)

D_o = dose rate found 1.5.1960

t = time /years/

d) Experimental dose rate determination (1.5.1960)

A solution of 0.40 g. $Fe_2(NH_4)_2(SO_4)_2.6\ H_2O$ (Analar), 0.06 g. NaCl (Analar) and 3.0 ml. H_2SO_4 conc. (Analar) was made up with water to 1 l. The water was London tap water, purified by two distillations from basic potassium permanganate and saturated with air by vigorous shaking. All tubes, flasks, pipettes involved in the operation were kept over night in chromic - sulphuric acid, rinsed with hot tap water for 10 min., six times with distilled water, six times with triple distilled water and three times with ferrous sulphate solution.

Irradiation: Pyrex-glass tubes (ø 1.8 cm.)[x], containing 10 ml. ferrous sulphate solution, were brought into four positions, equi-distant from the centre of the ^{60}Co -source and irradiated for periods of 15 min. or 30 min. respectively. A first series of sample solutions was discarded and the tubes rinsed twice with ferrous sulphate solution.

[x] ø = diameter

The absorption at 304 mμ of the irradiated solution against ferrous sulphate solution at 25(±0.1)°C. (Thermostat, Beckmann DU Spectrometer):

	E after irradiation		
sample	15 min.	30 min.	
1	0.345	0.680	
2	0.342	0.695	average E (15 min.)
3	0.338	0.670	0.344
4	0.355	0.700	

Absorbed dose (15 min.): 9476 rad

The calculated dose rate (for $Fe_2(NH_4)_2(SO_4)_2$ solution in 0.1 NH_2SO_4) was therefore (1.5.1960)

$$37900 \text{ rad/hr} = 2.365 \times 10^{18} \text{ eV/g}$$

e) Units and conversion factors in radiation chemistry.[16]

Units of dose

1 rad = 100 erg/g

$= 6.24 \times 10^{13}$ eV/g

$= 2.78 \times 10^{-9}$ watt.hr/g

1 roentgen(r) of hard X- or γ-radiation delivers 0.88 rad to air

1 roentgen(r) of hard X- or γ-radiation delivers 0.98 rad to water

1 rep = 84 or 93 ergs/cm^3 or erg/g, depending on definition

10^{14} eV/g = 1.60 rad

1 watt.hr/g = 3.60×10^8 rad

10^6 rad = 1 Mrad

Other units

1 eV = 1.602×10^{-12} erg

1 erg = 6.24×10^{11} eV

1 cal = 4.185×10^7 erg

1 watt= 6.24×10^{18} eV/sec

1 eV/molecule = 23.1 kcal. per g-mole

1 kcal./g-mole = 0.0433 eV/molecule

energy of quantum in keV = $12{,}395/\lambda$; λ in Å

1 curie = 3.700×10^{10} disintegrations/sec

Avogadro's number N = 6.025×10^{23}

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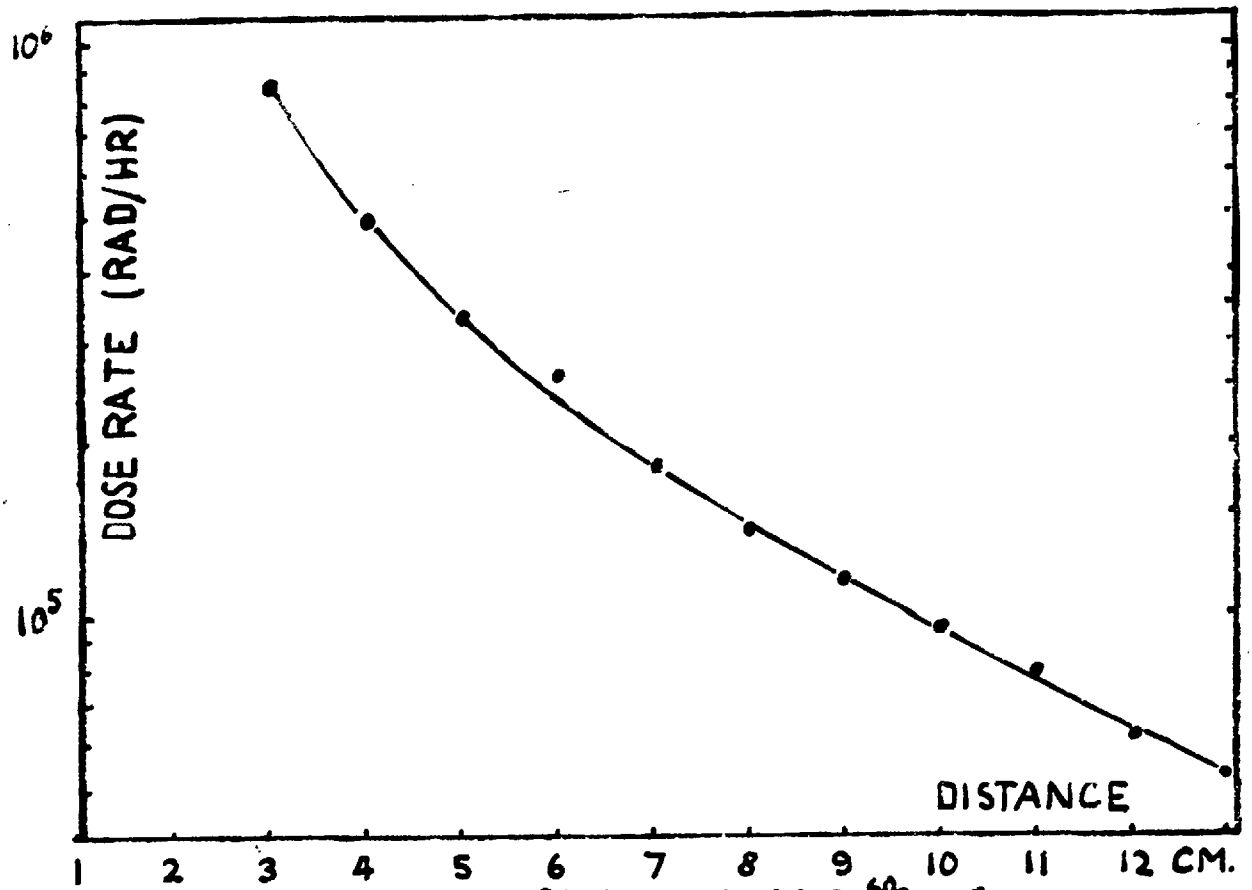


FIG. 2. CALIBRATION CURVE 1000 C ^{60}Co-Source

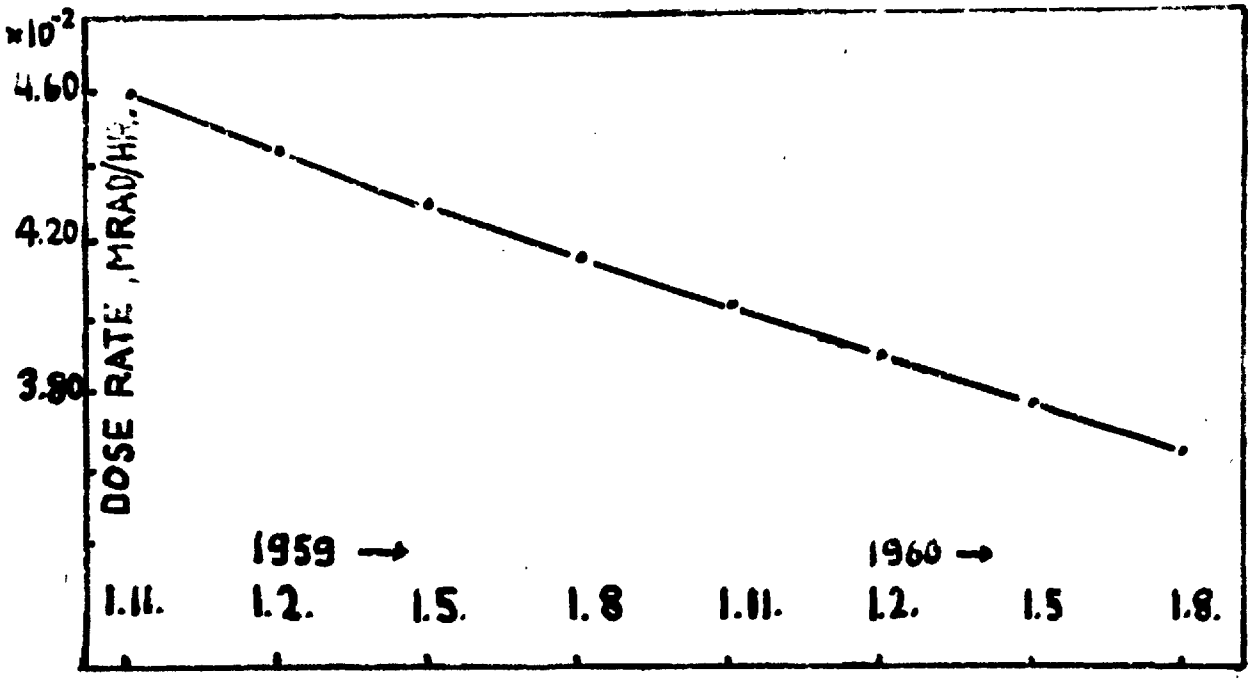


FIG. 1. DECAY OF DOSE RATE 80C ^{60}Co-Source
(DISTANCE 4 CM.)