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GLOW DISCHARGE POLYMERIZATION—II

α-METHYLSTYRENE, ω-METHYLSTYRENE AND ALLYLBENZENE

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Abstract—Previous work on the deposition of polymer on the electrodes of a radiofrequency glow discharge through styrene vapour has been extended to the examination of three other monomers. The mechanism proposed for styrene. involving the competitive reactions of radicals formed on the electrodes by electron bombardment, is applicable to the other monomers but it now appears that the radical recombination reaction can be neglected. It is not yet clear whether the propagation step involves the reaction of radicals with adsorbed monomer or with monomer diffusing to the electrode from the gas phase.

INTRODUCTION

IN PART I(1) of this work the deposition of polymer on the electrodes of a 2 MHz glow discharge through styrene vapour was investigated. The results were interpreted quantitatively on the basis of a simplified mechanism involving the competitive reactions of radicals formed on the electrodes by electron bombardment. Once polymer has been formed on the electrodes, it is subject to further irradiation by electrons during the time which the discharge operates. The mechanism postulated should be generally applicable and it is of interest to extend the study to other suitable monomers.

In the radiation chemistry(2) of polymers it is found that those with repeating units of the type $-[-CH_2—CHR-]-$ predominantly crosslink when irradiated whereas those with repeating units of the type $-[-CH_2—CR_1R_2-]-$ predominantly undergo chain scission. This contrast has been shown by polystyrene(3) and poly(α-methylstyrene)(4) and, as the glow discharge polymerization of styrene has already been studied,(1) the examination of α-methylstyrene and the isomeric ω-methylstyrene seems to be a useful extension.

It is also known that the attempted conventional radical polymerization of allylbenzene(5) can result in quantitative isomerization(6,7) to ω-methylstyrene with the possible formation of small amounts of poly(ω-methylstyrene). For these reasons the previous work with styrene has been extended to the examination of not only α-methylstyrene and ω-methylstyrene but also allylbenzene.

EXPERIMENTAL

The apparatus and technique were the same as described earlier.(1) The amount of polymer deposited on the electrodes was determined by weight and the molecular weights of soluble films of poly(α-methylstyrene) were determined from intrinsic viscosity measurements of toluene solutions at 25° using semi-micro Ostwald viscometers and employing the relation(8) $[\eta] = (7\cdot81 \times 10^{-5}) M^{0\cdot73}$.

The i.r. spectra of all three polymers were examined by removing the films from the electrodes and incorporating them in potassium bromide discs.

RESULTS

α-methylstyrene

Under most experimental conditions, fairly uniform pale yellow films were formed on the electrodes. At current densities less than 5 mA cm^{-2}, the deposits were shiny and transparent but at higher current densities they were generally opaque. Under harsh conditions, the polymer was somewhat degraded and adhered poorly to the substrate.

In general, the polymers obtained from α-methylstyrene were the most soluble encountered in this work. The films obtained at current densities of 5 mA cm^{-2} or less with short discharge times were readily soluble in a variety of solvents but, as the discharge time or the current density increased, the films became progressively more insoluble. Thus, products obtained at discharge times greater than 20 sec at 5 mA cm^{-2} were quite insoluble in benzene but those obtained after 60 sec at 3 mA cm^{-2} were still quite soluble. Most of the films obtained at 7 mA cm^{-2}, with the exception of those formed using very short discharge times ($<$ 10 sec), were insoluble.

At low current densities and short discharge times, the films obtained were tacky but hardened on exposure to air for several days. This ageing had little effect on the solubility.

As in the previous work with styrene,$^{(1)}$ it was not possible to determine mol. wts. of individual films as the amounts of material produced were too small. The increased solubility of α-methylstyrene films over styrene films, however, enabled the mol. wts. of polymers prepared at two different current densities to be determined. Bulk solutions of several polymer films prepared at each of the current densities 3 mA cm^{-2} and 5 mA cm^{-2} were made and their viscosity average mol. wts. were found to be 6300 ± 500 and 7400 ± 600 respectively.

The i.r. spectra of insoluble films of α-methylstyrene were not very informative but

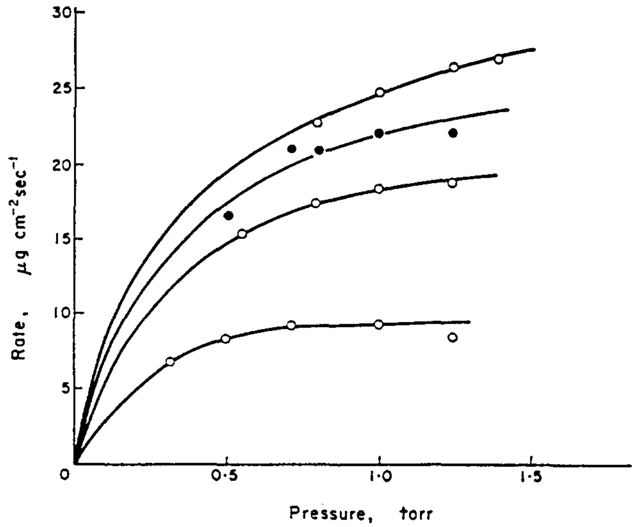

FIG. 1. Variation of rate of deposition of α-methylstyrene with pressure.
⊖ = 3·0 W cm^{-2}; ● = 2·3 W cm^{-2}; ○ = 1·9 W cm^{-2}; ⊙ = 1·2 W cm^{2}.

exhibited absorption bands at 3500 cm^{-1} and 1710 cm^{-1} which were attributed to the presence of —OH and $> C = O$ respectively, as in the styrene work.

The deposition of α-methylstyrene films has been studied as a function of time at fixed initial pressures and various current densities. The rates of deposition of polymer were usually similar to those encountered for styrene under comparable experimental conditions. At low powers, the rate of deposition is independent of time but, at higher powers, the rate falls off with time. In these latter cases, the significant rates of deposition are given by the tangents to the weight–time curves at the origin as these will be the rates corresponding to the known initial pressure of monomer.

The variation of the rate of deposition with pressure at various power ratings is shown in Fig. 1. To maintain consistency with the previous work, the power is expressed in W cm^{-2}, the product of current density and discharge voltage.

ω-methylstyrene

The experimental results for ω-methylstyrene were severely restricted by the low rates of deposition of the polymer at the discharge powers obtainable and by the persistent occurrence of corona discharge at current densities greater than 3 mA cm^{-2}. The polymer films were disrupted by common organic solvents but were insoluble so that it was not possible to determine mol. wts.

The i.r. spectra of the polymers were very similar to those of α-methylstyrene showing —OH and $> C = O$ absorption bands at 3500 cm^{-1} and 1710 cm^{-1} respectively.

The low rates of deposition and the corona problem limited the kinetic data which could be obtained. Weight–time graphs have been plotted for two discharge powers over a small range of initial pressures. The rates of deposition obtained from these plots are illustrated graphically in Fig. 2. The rates of deposition were approximately constant at both powers above a pressure of 0·5 torr. The graphs in Fig. 2 have been drawn to the origin although no results could be obtained at pressures less than 0·35 torr owing to the corona problem.

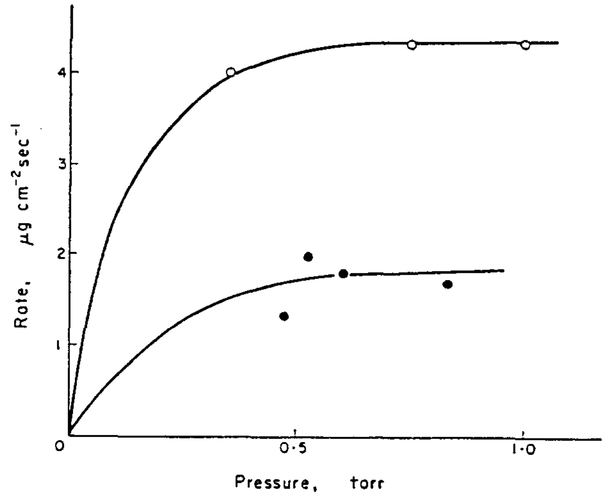

FIG. 2. Variation of rate of deposition of ω-methylstyrene with pressure.
○ = 1·2 W cm^{-2}; ● = 0·5 W cm^{-2}.

Allylbenzene

The polymer films obtained from allylbenzene were apparently the most uniform obtained in this work. At low current densities (< 2 mA cm^{-2}), shiny colourless films were obtained but, at higher current densities, the films were yellow. Under harsh conditions (7 mA cm^{-2}) and discharge times greater than 20 sec, some degradation of the films was apparent from their brown colour. Even under these conditions, the films seemed to be uniform and adhered well to the substrate.

Films prepared at current densities of less than 3 mA cm^{-2} were soluble in a variety of common organic solvents. Films prepared at 5 and 7 mA cm^{-2} were insoluble in common organic solvents but were readily disrupted.

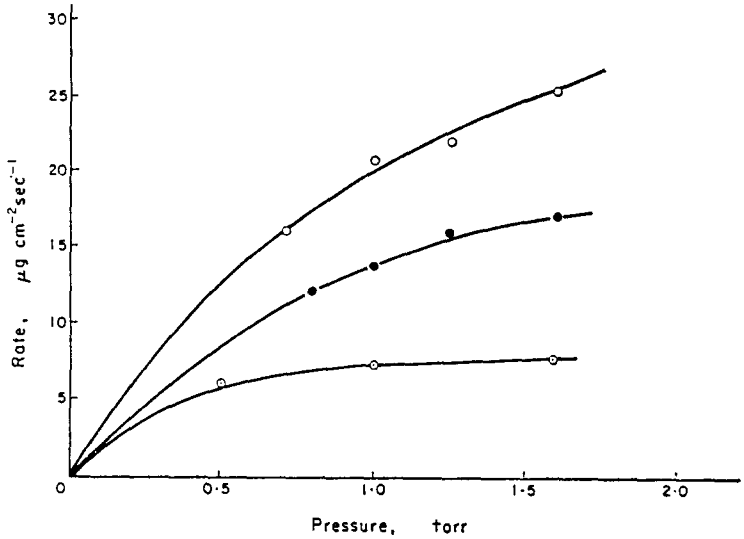

FIG. 3. Variation of rate of deposition of allylbenzene with pressure.
○ = 3·6 W cm^{-2}; ● = 2·4 W cm^{-2}; ⊙ = 1·2 W cm^{-2}.

The determination of mol. wts. for these films was not possible in the usual way because the values for the constants in the appropriate equation are not available.

The i.r. spectra of the allylbenzene films were similar to those of α- and ω-methylstyrene, showing the —OH and $>$ C = O bands at 3500 cm^{-1} and 1710 cm^{-1} respectively.

The deposition of the polymer has been studied as a function of time at various pressures and discharge powers; the rates of deposition deduced from the results are summarized in Fig. 3 where the rates are plotted as a function of pressure at three different discharge powers.

DISCUSSION

In the previous work with styrene,$^{(1)}$ it was shown that the polystyrene films contained trapped radicals and there was evidence that, on exposure to the atmosphere, the trapped radicals reacted with oxygen. The occurrence of absorption bands in the i.r. spectrum of the polystyrene corresponding to —OH and $>$ C = O was considered to be supporting evidence for the occurrence of this reaction. As these absorption bands occur in the spectra of the three polymers examined in the present work, it seems reasonable to conclude that once again trapped free radicals occur in all the polymer films.

The solubilities of the poly(α-methylstyrene) films are greater than those of the polystyrene films. This is probably due to the α-methyl substituent which will decrease the probability of crosslinking under similar experimental conditions. Although poly(α-methylstyrene) predominantly undergoes chain scission when irradiated, insoluble films of poly(α-methylstyrene) are obtained using sufficiently harsh discharge conditions. This shows that, although structural considerations have some bearing on the product, the rather violent method of glow discharge initiation of polymerization is probably the dominant factor.

The insolubility of all the poly(ω-methylstyrene) films, even under mild discharge conditions, indicates that they have a highly crosslinked structure. This polymer, having the possibility of forming two tertiary radicals per monomer unit, viz. $-[-\mathrm{CHMe{-}CHPh}-]- \xrightarrow{\rightsquigarrow} -[-\dot{\mathrm{C}}\mathrm{Me}{-}\dot{\mathrm{C}}\mathrm{Ph}-]-$, might be expected to show a high degree of crosslinking on irradiation.

In contrast to the insolubility of all the poly(ω-methylstyrene) films, the films formed from allylbenzene at low current densities were soluble. It thus seems that this process gives a polymer of allylbenzene rather than an initial isomerization to ω-methylstyrene followed by the polymerization of this monomer.

As the violence of glow discharge polymerization can lead to fragmentation of the original monomer and the incorporation of these fragments into the polymer, any consideration of the detailed structures of the polymer films will be somewhat speculative. There is some justification, however, for assuming that the films do contain some proportion of the normal addition polymer structure. With prolonged discharge times or with high current densities, some degradation of the polymer films was shown by their colouration. Under similar experimental conditions, this colouration was more intense in the case of polymer derived from allylbenzene than for those polymers derived from styrene and the substituted styrenes. In the styrene polymers, the aromatic nuclei are attached directly to the polymer chain and should exert a protective effect(9) whereas, in the normal polyallylbenzene structure, $-[-\mathrm{CH(CH_2Ph){-}CH_2}-]-_n$, the aromatic nucleus is not directly connected to the polymer chain and cannot be nearly so effective in protecting the polymer against radiation damage.(10)

It has been previously proposed(1) that electron bombardment of the film on the electrodes produces radicals which can then react in three ways.

$$\mathrm{R}_n^{\cdot} + \mathrm{M} \rightarrow \mathrm{R}_{n+1}^{\cdot} \tag{i}$$

$$\mathrm{R}_n^{\cdot} + \mathrm{R}_m^{\cdot} \rightarrow \mathrm{P}_{n+m}\ (\text{or } \mathrm{P}_n + \mathrm{P}_m) \tag{ii}$$

$$\mathrm{R}_n^{\cdot} \rightarrow \mathrm{R}_n^{\cdot}\ (\text{trapped}). \tag{iii}$$

This reaction scheme gives the rate of deposition of polymer as

$$\text{Rate} = r.\frac{p}{p + k_2\,[\mathrm{R}^{\cdot}]/kk_1 + k_3/kk_1} \tag{1}$$

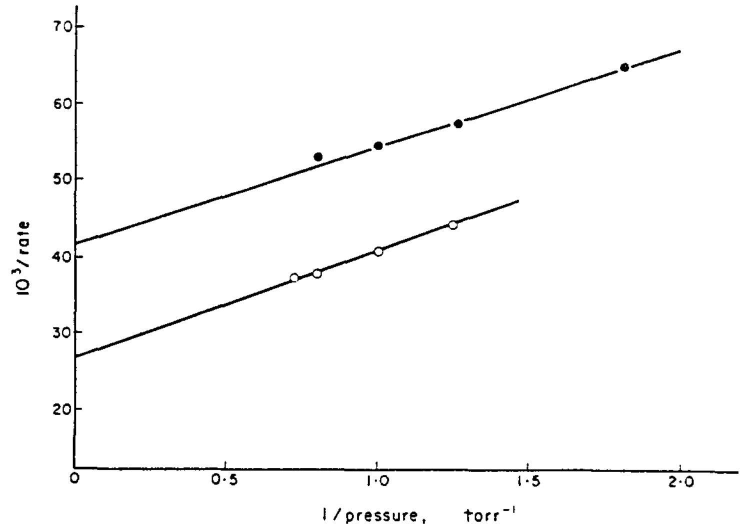

FIG. 4. Reciprocal rate against reciprocal pressure for α-methylstyrene. ● = $1\cdot9$ W cm^2; ○ = $3\cdot0$ W cm^{-2}.

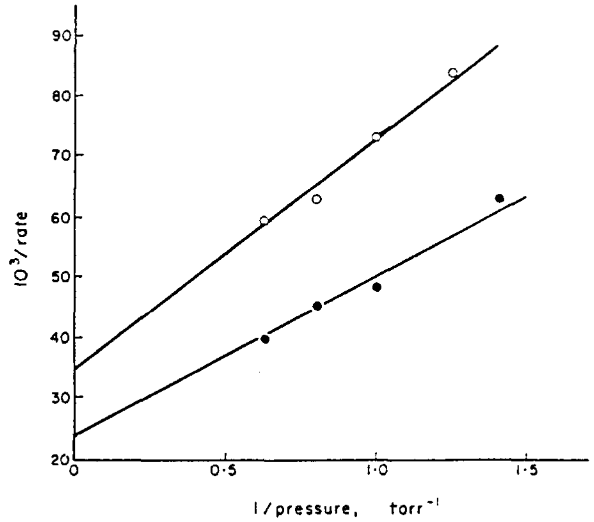

FIG. 5. Reciprocal rate against reciprocal pressure for allylbenzene. ○ = $2\cdot4$ W cm^{-2}; ● = $3\cdot6$ W cm^{-2}.

where r is the rate of production of radicals in μg cm^{-2} sec^{-1}, k_1, k_2 and k_3 are the rate constants of reactions (i), (ii) and (iii) respectively, [R$^\cdot$] is the stationary concentration of radicals, p is the pressure and k is the proportionality constant relating the concentration of monomer in the above reactions to the pressure.

Equation (1) shows that at high pressures the rate of deposition should tend to a limiting value of r. Inverting Eqn. (1) gives

$$\frac{1}{\text{Rate}} = \frac{1}{p}\left(\frac{k_2\,[\mathrm{R}^\cdot]/kk_1 + k_3/kk_1}{r}\right) + \frac{1}{r}. \tag{2}$$

[R$^\cdot$] should be constant for a given discharge power and a lot of 1/Rate against $1/p$ should be a straight line of intercept $1/r$. These reciprocal graphs have been potted for α-methylstyrene and allylbenzene; two representative cases for each monomer are illustrated in Figs. 4 and 5 respectively. The values of r for the discharge powers investigated in each case are given in Table 1.

TABLE 1. LIMITING RATES AT HIGH PRESSURES

Power, W ($\mathrm{W\ cm^{-2}}$)	Limiting rate, r ($\mu\mathrm{g\ cm^{-2}\ sec^{-1}}$) α-methylstyrene	 allylbenzene
1·20	15·0	
1·23		8·93
1·94	24·0	
2·30	28·8	
2·40		29·0
3·00	37·6	
3·60		42·4

The limiting rates given in Table 1 are equal to the rates of production of radicals at the powers quoted. In Part I(1) of this work, an attempt was made to interpret the relation between r and W. Further consideration shows that this attempt was somewhat naïve. A calculation of the amplitude of oscillation of the electrons in the discharge used gives an amplitude of about 40 cm. As the separation of the electrodes was 2·3 cm the discharge will be operating in the transition region between the resonance condition and the diffusion régime.(11) Under these conditions, the relationship between the energy transferred to the electrodes by electron bombardment and the average power, W, of the discharge will be extremely complex. It is thus very difficult to interpret the relation between r and W; r is probably best expressed empirically as a power function of W

$$r = k'W^n. \tag{3}$$

To obtain a value of [R$^\cdot$] for Eqn. (1), the stationary state treatment is applied to the radicals. As before,(1) Eqn. (1) reduces to

$$\text{Rate} = r.\frac{p}{p + A + \sqrt{(A^2 + Br)}} \tag{4}$$

where $A = k_3/2kk_1$ and $B = k_2/k^2k_1^2$.

Denoting the slopes of the reciprocal graphs (as exemplified in Figs. 4 and 5) by S, from Eqn. (4)

$$rS = A + (A^2 + Br)^{\frac{1}{2}}$$

whence

$$rS^2 = 2AS + B.$$

Plots of rS^2 against $2S$ are shown in Figs. 6 and 7 for α-methylstyrene and allylbenzene respectively. The intercept on each graph should give the value of B for each monomer.

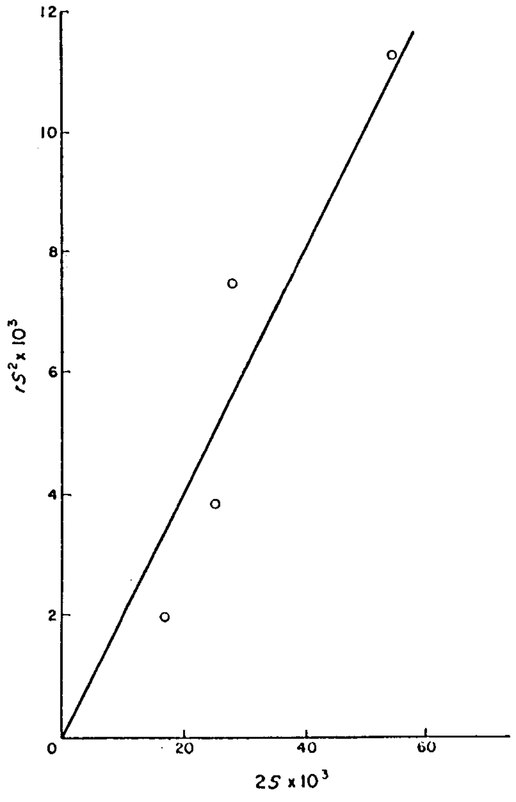

FIG. 6. rS^2 against $2S$ for α-methylstyrene.

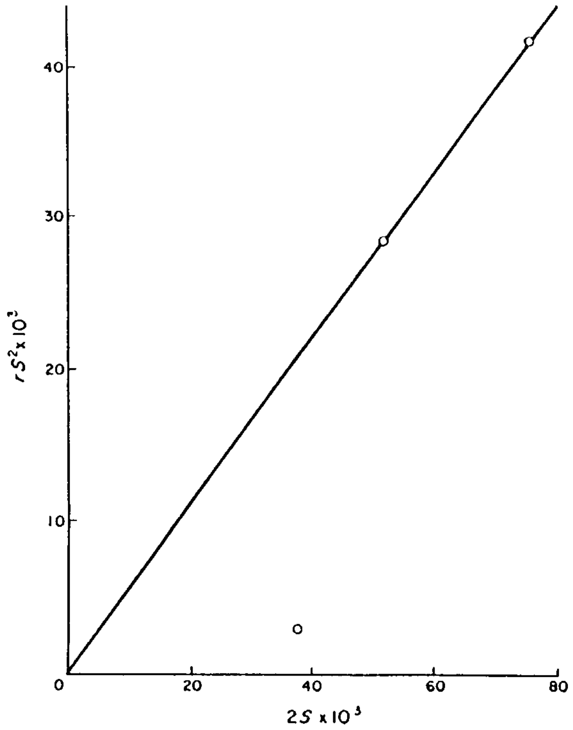

FIG. 7. rS^2 against $2S$ for allylbenzene.

As B cannot be negative, the graphs have been drawn to the origin. Thus, the graphs give

α-methylstyrene	$A = 0{\cdot}20$	$B = 0$
allylbenzene	$A = 0{\cdot}55$	$B = 0.$

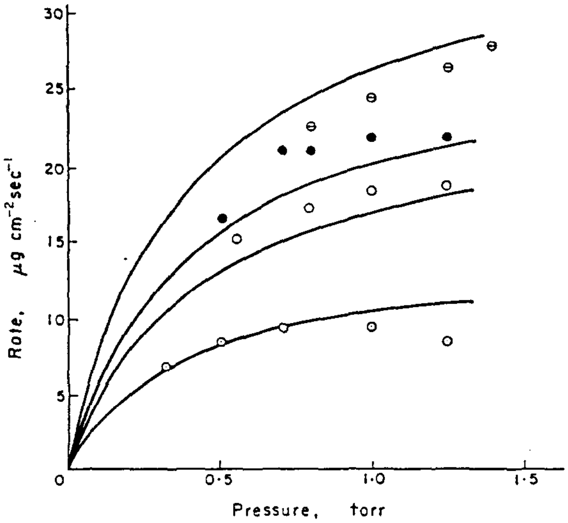

FIG. 8. Comparison of calculated and experimental results for α-methylstyrene. Experimental: ⊖ = 3·0 W cm^{-2}; ● = 2·3 W cm^{-2}; ○ = 1·9 W cm^{-2}; ⊙ = 1·2 W cm^{-2}. Calculated: ——————

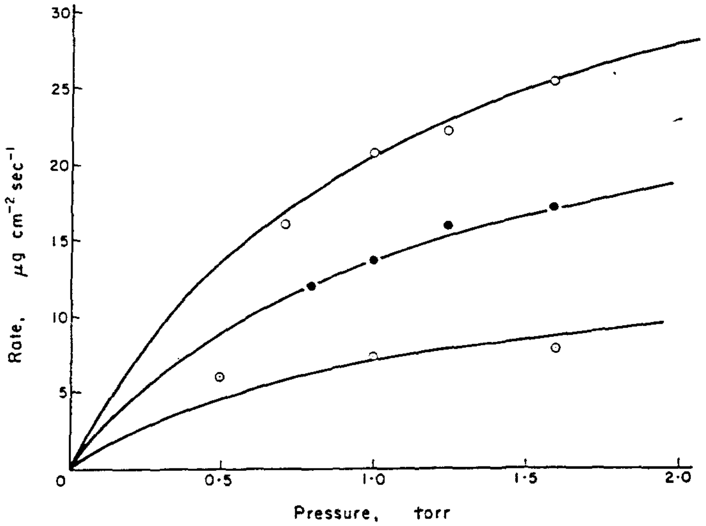

FIG. 9. Comparison of calculated and experimental results for allylbenzene. Experimental: ○ 3·6 W cm^{2}; ● = 2·4 W cm^{-2}; ⊙ = 1·2 W cm^{-2}. Calculated: ——————

The implication of these results is that k_2 is negligible compared with k_1 and that reaction (ii) is unimportant. If B is taken as zero, Eqn. (4) takes the form

$$\text{Rate} = r.\frac{p}{p+2A}. \tag{6}$$

Using the values of A derived from Eqn. (5) together with the values of r from Table 1, Eqn. (6) can be used to calculate the rates of deposition of material at various pressures for the discharge powers investigated for each monomer. These calculated values are compared with the experimental results in Figs. 8 and 9. A plot of the logarithms of the values of r from Table 1 against log W for each monomer gives

$r = 12{\cdot}3\ W$ for α-methylstyrene

$r = 12{\cdot}0\ W$ for allylbenzene.

Putting these relationships in Eqn. (6) with the appropriate values of A gives, for a pressure of 1·25 torr,

$$\text{Rate} = 9{\cdot}32\ W \quad \text{for } \alpha\text{-methylstyrene} \tag{7}$$

$$\text{Rate} = 6{\cdot}38\ W \quad \text{for allylbenzene.} \tag{8}$$

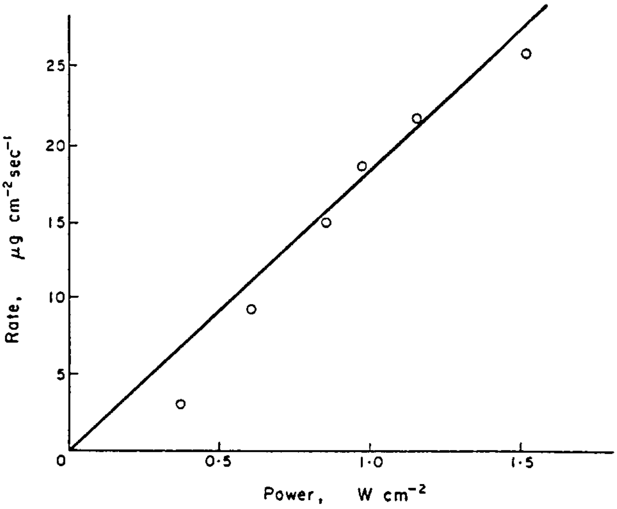

FIG. 10. Comparison of calculated and experimental results for α-methylstyrene at 1·25 torr. Experimental: ○; Calculated: ———

The rates of deposition for each monomer have been determined over a range of discharge powers at 1·25 torr; in Figs. 10 and 11, the results are compared with the rates predicted from Eqns. (7) and (8).

The experimental and calculated results for α-methylstyrene are of the same form but the agreement is not very good. If the propagation reaction proceeds by a radical reacting with an adsorbed monomer molecule, the best way of representing the monomer concentration is by means of the BET equation. This equation, however, is only valid up to relative pressures of about 0·4. The vapour pressure of α-methylstyrene

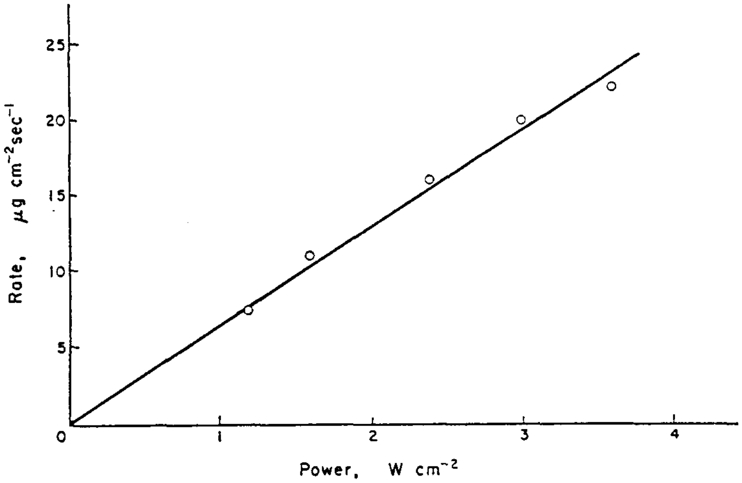

FIG. 11. Comparison of calculated and experimental results for allylbenzene at 1·25 torr. Experimental: ○; Calculated: ————

at 25° is about 2·2 torr and the polymerization has been investigated up to pressures of 1·4 torr. The limits of validity of the BET equation have thus been exceeded and, if the propagation proceeds preponderantly through adsorbed monomer, the disparity between experimental and calculated results is not surprising.

In contrast, the agreement between the experimental and calculated results for allylbenzene is excellent. The vapour pressure of allylbenzene at 25° is about 1·8 torr and experiments have been carried out with this monomer at pressures up to 1·6 torr. Once again the limits of validity of the BET equation have been exceeded. The implication might be that in this case propagation proceeds through the reaction of a radical with monomer diffusing to the electrode from the gas phase although this conclusion must be considered highly speculative in view of the paucity and indirect nature of the evidence. A further complicating factor in this case is the possible isomerization of allylbenzene to ω-methylstyrene although the behaviour of allylbenzene in the discharge is vastly different from that of ω-methylstyrene.

In general, the mechanism invoked to explain the results for styrene seems to apply fairly satisfactorily to the deposition of allylbenzene and α-methylstyrene films although there are points of detail which are still obscure. In the latter two cases, a value of zero for the constant B indicates that the recombination reaction is of little importance; this may also be considered to be true in the case of styrene where $B = 0{\cdot}01$ and $A = 0{\cdot}28$.(1) The principal remaining problem is whether the propagation step involves adsorbed monomer or not; it is hoped that further work may shed some light on this question.

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Résumé—On a étendu à l'examen de trois nouveaux monomères l'étude du dépôt de polymère sur les électrodes observé au cours d'une décharge de radiofréquence à travers la vapeur du styrène. Le mécanisme proposé pour le styrène, mettant en jeu une compétition de réactions des radicaux formés sur les électrodes par le bombardement électronique, est applicable aux autres monomères mais on s'aperçoit maintenant que la réaction de recombinaison radicalaire peut être négligée. On ne peut pas encore affirmer clairement si le processus de propagation met en jeu la réaction de radicaux avec le monomère adsorbé ou avec le monomère diffusant vers les électrodes à partir de la phase gazeuse.

Sommario—Lavori precedenti sulla deposizione di polimero sull'elettrodo di una discarica a bagliore di radiofrequenza attraverso vapori di stirene sono stati estesi all'esame di tre altri monomeri. Il meccanismo proposto per lo stirene, richiamante le reazioni competitive di radicali formati sugli elettrodi dal bombardamento elettronico, è applicabile agli altri monomeri ma sembra ora che la reazione di ricombinazione dei radicali può essere tralasciata. Non è ancora ben chiaro se il passo di propagazione richieda la reazione di radicali con monomero adsorbito o con monomero diffondentesi sull'elettrodo dalla fase gassosa.

Zusammenfassung—Frühere Arbeiten über die Ablagerung von Polymeren auf den Elektroden bei Radiofrequenz-Glimmentladung in Styroldampf wurden auf drei weitere Monomere ausgedehnt. Der für Styrol vorgeschlagene Mechanismus mit kompetitiven Reaktionen der beim Elektronenbeschuß an den Elektroden gebildeten Radikale ist auch auf die andern Monomeren anwendbar, aber es scheint jetzt, daß die Rekombinationsreaktion der Radikale vernachlässigt werden kann. Es ist aber noch nicht klar, ob der Wachstumsschritt durch Reaktion der Radikale mit adsorbiertem Monomerem zustandekommt, oder mit Monomerem, das aus der Gasphase an die Elektroden diffundiert.