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RADIATION INDUCED IONIC POLYMERIZATION AND GRAFTING OF VINYL MONOMERS

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Abstract - Some special aspects of the radiation induced ionic polymer-
ization and grafting of vinyl monomers will be described. In particular
the effects of solvents on the cationic polymerization of the vinyl
ethers will be discussed in detail. The unequivocal free ion nature
of the polymerization makes such information of considerable general
interest. Estimates of the propagation rate constants with free cation
polymerization in solvents of different dielectric constants and
solvation powers will be presented. Finally, some observations on the
radiation induced graft polymerization of ethyl vinyl ether to poly(vinyl
chloride) and to polypropylene will be presented.

INTRODUCTION

The polymerization of liquid vinyl monomers with high energy radiation has been studied
since, at least, 1938. It was shown in the classical studies of Dainton and others that
the mechanism was of a free radical nature (1). However, Davison, Pinner and Worrall (2)
in 1957 successfully polymerized isobutylene in the liquid state at $-78°C$ with high energy
radiation. This was probably the first demonstration that an ionic polymerization could
be initiated in the liquid state using high energy radiation. After considerable research
by a number of workers including Williams, Hayashi, Okamura, Metz, Chapiro and the present
author, an acceptable picture of this type of radiation polymerization has been developed (3).

Briefly, it is believed that those few free ions which escape geminate recombination initiate
cationic polymerization by a free ion mechanism. The chains propagate in the same way and
eventually terminate either by reaction with an impurity or by combination with the negative
species of unknown structure. The yield of free ions is low, about 0.15 per 100 eV, and the
propagation rate very high. For these reasons the kinetic chains lengths are very large
in spite of the high rate constant for chain termination. Similarly the stationary concen-
tration of growing chains is very low, about 10^{-10} moles per liter. For these reasons the
effect of even minute amounts of impurity is very important.

The effect of impurities, believed in general to be water, is more serious than with
chemical systems due to their constant regeneration by the following type of reaction:

$$H_3O^+ + Y^- \longrightarrow H_2O + YH$$
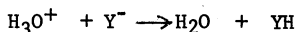
where H_2O is the impurity and Y^- the negative species. The molecular weights of the re-
sulting polymers could be low, in spite of the large kinetic chain length, due to chain
transfer to monomer. Although the above discussion suggests positive ion propagation, in
rarer instances, such as with nitroethylene, negative (carbanion) polymerization can take
place.

In an elegant kinetic treatment Williams et alia (4) derived the following rate expression:

$$Rp = \frac{R_i \cdot k_p(M)}{(R_i k_t)1/2 + k_x(X)} \qquad (1)$$

Where R_p is the rate of polymerization, R_i the rate of initiation, k_t the rate constant
for termination by combination with species of the opposite charge, k_x the rate constant
for reaction of the growing chains with an impurity, X, and (M) and (X) the concentrations
of monomer and impurity, respectively.

Since $R_i = K$ (Dose Rate) it is clear that at high impurity levels the rate becomes pro-
portional to the dose rate. At zero impurity level, however, the rate is proportional to

the square root of the dose rate. Also, and most importantly from the point of view of the use of accelerators, as the dose rate increases the effect of impurities decreases. This means that, in principle, the ionic mode can be induced at high dose rates even with monomers which have not been rigorously dried. This has also been confirmed in practice. It could be asked, why should one be interested in inducing ionic reactions with radiation? There are two practical reasons, apart from the obvious fundamental interest. (1) a number of useful monomers such as isobutylene, vinyl ethers, α-methyl styrene and others only polymerize by an ionic route. (2) the rate constants for chain propagation are very high with free ionic growth. Styrene, for example, has a cationic rate constant at room temperature of about 10^6 M^{-1} s^{-1} compared with only 30 for free radical growth. The vinyl ethers, which have the lowest ionic rate constants, are still in the 10^3 - 10^5 range. This means that even with the high dose rates associated with electron accelerators substantial polymerization before termination can take place, isobutylene being a good example.

The fundamental interest in radiation induced ionic polymerization stems from the unequivocal free ion nature of the reaction. It can be seen from equation 1 that in the complete absence of impurities the rate expression reduces to

$$R_p = k_p \ (M) \ \left(\frac{R_i}{k_t} \right)^{\frac{1}{2}} \qquad\qquad (2)$$

Reasonable estimates of R_i and k_t can be obtained from electrical conductivity measurements of the monomer in the radiation field and from simple theoretical considerations (4,5). These combined with rate measurements lead to estimates of the propagation rate constants, k_p, for the free ion polymerization process. Estimates can also be made with chemical initiation, mainly using stable carbonium ion salts, pioneered by Bawn, Ledwith and co-workers (6) and later extended and refined by Sigwalt and co-workers (7,8).

The author and his colleagues have conducted extensive studies on radiation induced cationic polymerization and, in the case of the vinyl ethers, parallel studies initiated with stable carbonium ion salts. Some of the more significant findings resulting from this work will be presented in this paper. In addition to homopolymerization some radiation induced ionic grafting studies will be presented.

POLYMERIZATION STUDIES

p-Methoxy Styrene. Radiation induced ionic polymerization studies can provide useful additional information taken in conjunction with results obtained with chemically initiated systems. For example, there is little or no activation energy associated with either the rates of initiation or termination. This can lead to direct estimates of the energy of activation for the propagation reaction. In the case of p-methoxy styrene two groups have studied in detail its chemical initiated polymerization in methylene chloride solution using trityl (8) and cycloheptatrienyl (9) hexachlorantimonates as catalysts. The former workers (8) found a negative activation energy for propagation of 5.6 kcals per mole and the latter (9) a positive value of 4.8 kcals/mole. The radiation polymerization in bulk and in methylene chloride solution has been studied in these laboratories (10). The results are summarized in Table 1.

TABLE 1.   Propagation rate constants, k_p, and activation energies, Ea, for the "free" cationic polymerization of styrene, α - methyl styrene and p-methoxy styrene.

Monomer	Initiator	Temperature	k_p M^{-1} s^{-1} x 10^{-6}	Ea Kcals.mole^{-1}	Reference
Styrene	Radiation	15°C	3.5	~ 0	4,5
α-Methyl styrene*	"	0°C	3.4	~ 0	4,5
p-Methoxy styrene*	"	"	3.0	~ 0	10
p-Methoxy styrene**	"	"	-	~ 0	10
"	$C_7H_7SbCl_6$	"	0.0036	+4.8	9
"	Ph_3SbCl_6	+10	0.028	-5.6	8

*bulk monomer   ** in CH_2Cl_2 solution

Activation energies of close to zero were found, in agreement with the results found with α-methyl styrene and styrene (5). The results indicate that the explanations offered by Sigwalt et al. (8). that the activation energies are probably due to the complex temperature dependencies of the initiation reactions are probably valid. The explanation of Goka and Sherrington (9) that the positive activation energy is due to the increased stability of the free p-methoxy styryl cation compared with styrene is not supported by the radiation studies. It is not possible to give more than a rough estimate of the propagation rate constants themselves with radiation initiation in solvents. This is due to the complexities involved in evaluating the initiation rates. However, the actual rates of polymerization were definitely much lower in methylene chloride than in bulk, in agreement with the chemical studies and dependent on the monomer-solvent ratio. The effects of solvents on free cation polymerization have been investigated in detail with the radiation initiated polymerization of the vinyl ethers under super-dry conditions and the results will be discussed in the next section of this paper.

The Vinyl Ethers. The vinyl ethers are particularly suitable for detailed study whether initiated with stable carbenium ion salts or with radiation. They respond well to the former and are somewhat easier to superdry than the hydrocarbon monomers. Early work with a number of vinyl ethers showed discrepancies between the estimated rate constants obtained by chemical initiation in methylene chloride solution and with radiation in bulk although in the case of isobutyl and ethyl vinyl ethers, reasonable agreement was found. The activation energies, on the other hand, agreed rather well in each case, certainly within the experimental error (11).

Apart from the inherent complexities and various assumptions made in both the chemical and the radiation methods in estimating the propagation rate constants, the overriding difference was that the chemical studies were conducted in methylene chloride solution whereas the radiation were in bulk. Considerable efforts have therefore been made recently to study the effect of solvents on the radiation initiated polymerization of ethyl vinyl ether and isopropyl vinyl ether (12). These showed the greatest differences in behaviour, as illustrated in Table 2, for example.

TABLE 2. Estimated propagation rate constants, k_p, at $0°C$ and activation energies, E_p, for the radiation initiated polymerization in bulk and chemically initiated polymerization in methylene chloride of ethyl and isopropyl vinyl ethers.

Monomer	Radiation (bulk)		Chemical (CH_2Cl_2)	
	k_p $M^{-1}sec^{-1} \times 10^{-4}$	E_p $Kcals.mole^{-1}$	k_p $M^{-1}sec^{-1} \times 10^{-4}$	E_p $Kcals.mole^{-1}$
Ethyl Vinyl Ether	1.42 ± 0.2	10.6 ± 0.2	0.61 ± 0.2	10.4 ± 0.4
Isopropyl Vinyl Ether	$90.9 + 0.2$	1.8	0.48*	3.2
Isopropyl Vinyl Ether	-	-	1.12**	3.5
Isobutyl Vinyl Ether	3.8	7.6	1.48	7.0 ± 0.1
t-Butyl Vinyl Ether	5.0	4.9	0.35	~ 2

*The highest value obtained with rigorous drying and assuming complete dissociation of the ions and no termination (11).

**Rate constants obtained by Subira, Sigwalt et al. (12) with a complete kinetic analysis.

Ethyl vinyl ether which appeared to be particularly well behaved has been studied in detail, isopropyl vinyl ether is currently under investigation in depth. The experimental details have been described elsewhere. The methods of estimating the initiation and termination rate constants in radiation are also discussed in detail elsewhere. The termination rate constants are probably quite reasonable estimates but the initiation rates are subject to some error. However, both enter into the rate expression (equation 2) to the one half power which helps, at least, to overcome any deficiencies.

The results with both ethyl and isopropyl vinyl ethers showed a strong dependence of the estimated propagation rate constants on the solvent. The rate constants were greatly reduced as the dielectric constant of the solvent increased. These results are shown plotted as $\ln. k_p$ versus $1/D$ where D is the bulk dielectric constant of the particular monomer-solvent mixture, in 50:50 mixtures by volume. A good linear relationship was shown, Fig. 1,

in agreement with the theory of Laidler and Eyring (13) for ion-molecule reactions. Similar results have been reported by Penczek et al. (14-17) with chemically initiated ring opening polymerizations. The actual expression derived by Laidler and Eyring was

$$\frac{d\ (\ln k)}{d\ (1/D)} = \frac{(ze)^2}{2\ KT}\ \left(\frac{1}{r} - \frac{1}{r^*}\right)$$

where ze is the charge on the ion, K and T the Boltzman constant and absolute temperature respectively, r and r^* are the radii of the ions in the original and activated complex states respectively. Since r^* can be expected to be larger than r a plot of ln.k versus 1/D should be linear and with a positive slope, i.e., the lower the dielectric constant the higher the rate. This is what was actually observed in this work.

Rigorously, local rather than the bulk dielectric constants should be used but these are not known. The early work gave some indication of a zero order polymerization, this would be in keeping with solvation of the growing cation with the monomer. This had also been postulated by Hayashi et al. (18) as a possible reason for the high activation energies often found with the vinyl ethers compared with hydrocarbon monomers, compare Tables 1 and 2, for example. Recently the order of the reaction rate on the monomer concentration has been examined in detail with ethyl vinyl ether.

Rate Studies. The conversion curves for ethyl vinyl ether in bulk (D $\sim$ 3.9) and in benzene (D $\sim$ 2.64) solutions, plotted as first order reactions, are presented in Fig. 2.
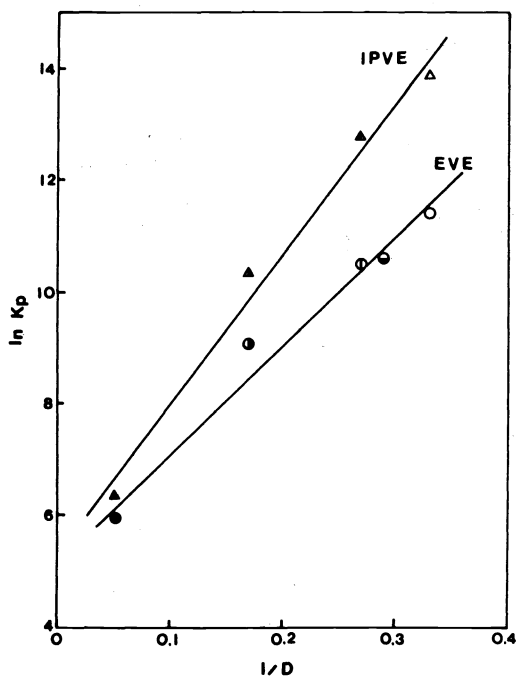

Fig. 1. Ln. k_p versus 1/D for radiation polymerization of ethyl and isopropyl vinyl ethers in various solvents. 50% by volume. Increasing D, bulk, diisopropyl ether, diethyl ether, methylene chloride and nitro methane at 30°C.
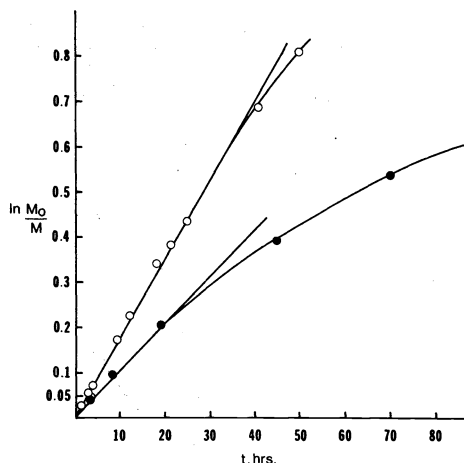
Fig. 2. First order plots of radiation polymerization of ethyl vinyl ether O, in bulk at 20°C ● in benzene $(M)_o$ = 3.1 M at 30°C.

In the bulk system the internal order is equal to unity with small deviations at very high conversions probably due to viscosity effects. In benzene however the order is more complex. Initial rates were determined and also changes in the k_t and R_i values with composition were estimated, from these (C^+) values were calculated, changes of less than a factor of two were found across the whole range of compositions studied. Details of the methods used will be published elsewhere.   A log-log plot of Rp/(C+) versus $(M)_o$ is given in Fig. 3. Except at high conversions an order of 1.25 was found. Without going into all the reasoning it was concluded that solvation by the polymer chains was taking place.   The activation energies were similar for example in bulk and in benzene solutions. Solvation by the polymer chains is also indicated by the similar estimated k_p values in a number of hydrocarbon and ether solvents, see Table 3 for example.

TABLE 3. Rates of polymerization, estimated free ion yields and rate
constants of polymerization in the radiation induced poly-
merization of EVE in low dielectric constant, D, solvents.
$T^O = 30^{\circ}C$ dose-rate 71 rad.s^{-1}

Solvent	D	$(M)_o$	$R_p \times 10^5$	G_i [a] $(\frac{\text{free ions}}{100 \text{ ev}})$	$k_p^c \times 10^4$
neo-Pentane	2.39	5.2	3.6	0.20 (0.50)[b]	6.0 (2.4)[b]
n-Pentane	2.42	5.2	2.5	0.14	3.8
Benzene	2.64	5.3	2.2	0.09_5	4.4
EVE (bulk)	$\sim$ 3	10.5	9.5	0.14	6.0
Diisopropyl ether	3.7	5.2	3.2	0.21	3.1
Diethyl ether	3.9	5.2	2.9	0.23	2.6

a) calculated by Allen method, the other method gives very similar values,
   except for neo-pentane
b) value determined by the simple additivity method and corresponding k_p value
c) determined from equation (1) assuming an order close to one in monomer for
   the reaction. This was checked for benzene and diethyl ether.

The introduction of highly polar or solvating molecules such as methylene chloride, on the
other hand, causes drastic changes in the rate and presumably destroys the solvation of the
growing cation by the polymer. In methylene chloride solution a first order reaction was
observed (Fig. 4) except at very high conversions where small additions of solvent decreased
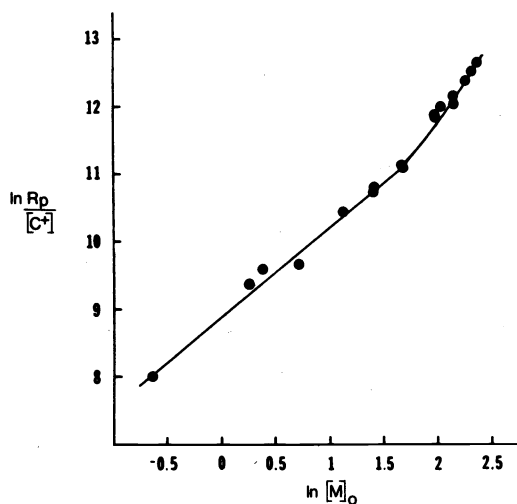the rate drastically.

Fig. 3. Ln. $R_p/(C^+)$ versus ln. (M_o)
for radiation polymerization of
ethyl vinyl ether in benzene at
$20^{\circ}C$, incl. bulk. (C^+) = steady state
concentration of growing cations.

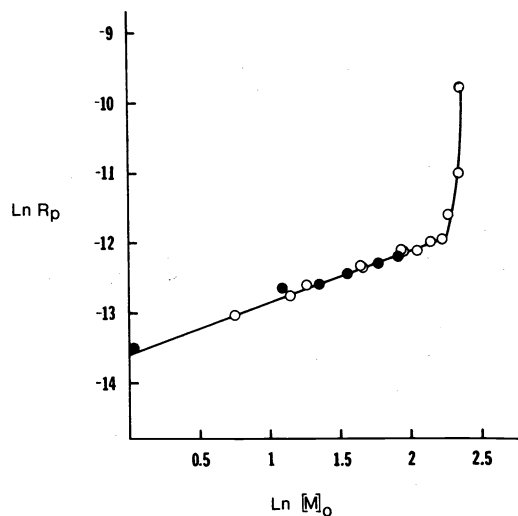Fig. 4. Ln. R_p versus ln. $(M)_o$
for radiation polymerization
of ethyl vinyl ether in o methy-
lene chloride and in $\bullet$ iso-
dielectric mixtures of ethyl
vinyl ether, benzene and methylene
chloride at $22^{\circ}C$, incl. bulk

Included in Fig. 4 are a number of iso-bulk-dielectric constant mixtures (D ~ 5) made up of EVE, benzene and methylene chloride. These fitted the same curve and, together with other results, clearly does not agree with the dielectric constant effects found earlier with simple 50:50 mixtures. The activation energies in pure methylene chloride and in the mixtures with benzene were about 8 kcals per mole compared with about 13.5 kcals per mole in bulk and in benzene. These presumably reflect the differences in the solvation by the methylene chloride and by the polymer chain respectively. Finally, comparative rate studies were conducted in two ethers with different dielectric constants and solvating power for the ions, diethyl ether and diglyme.

The rates adjusted for the estimated (C^+) values are presented as log-log plots of $R_p/(C^+)$ versus (M_o) in Fig. 5.
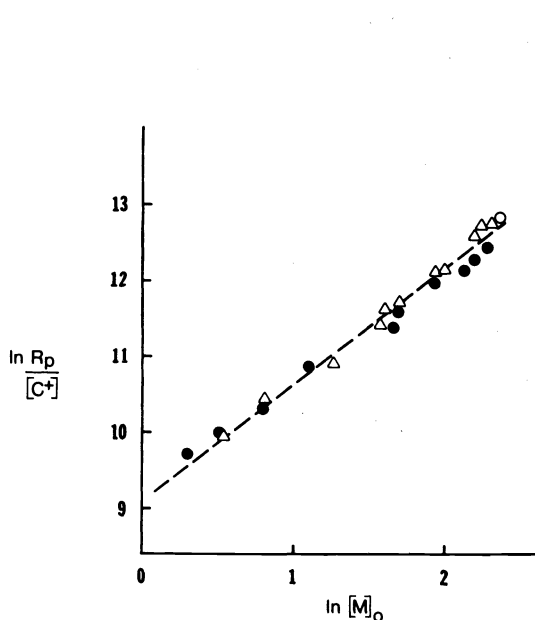

Fig. 5. Ln. $R_p/(C^+)$ versus ln. $(M)_o$ for radiation polymerization of ethyl vinyl ether in diethyl ether ●, diglyme △ and benzene (dashed line) at 23°C.
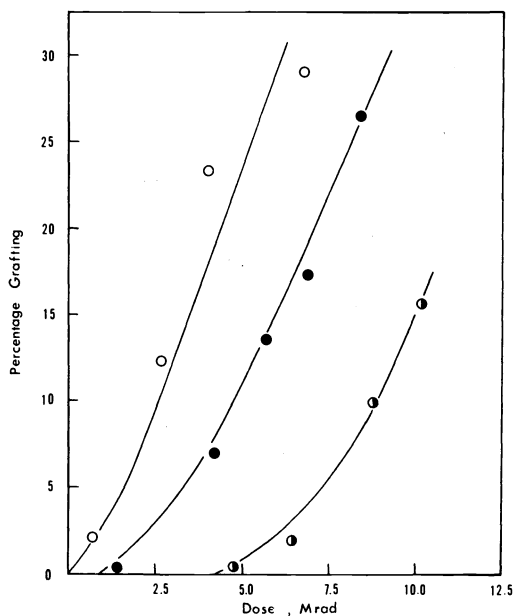
Fig. 6. Dose dependency of percentage grafting in radiation-induced grafting of EVE onto PVC powder at 50°C, dose rate 0.70 Mrad/hr: O superdry; ● dry; ◑ wet.

The results previously found with benzene are also included. Within experimental error the values all fall on the same line with a reaction order of 1.4 with respect to the initial monomer concentration. This value is somewhat high and could reflect some consistent problem with respect to the calculation of the (C^+) values. The activation energies were determined in diethyl ether and are presented in Table 4 together with those obtained with benzene, methylene chloride and in bulk.

TABLE 4. Activation energies in the radiation-induced polymerization
          of EVE in bulk and in solution.

Solvent	Monomer concentration M	Ea kcal.mole^{-1}
Bulk	10.5	13 ± 0.5
Benzene	5.4	13.5 ± 0.5
Benzene	2.1	13.5 ± 0.5
Diethyl ether	6.9	11.6 ± 0.5
Diethyl ether	5.3	11.5 ± 0.5
Diethyl ether	2.9	12.3 ± 0.5
Methylene dichloride	5.2	7 ± 1
Methylene dichloride + Benzene	5.2	8 ± 1

The values obtained with diethyl ether are quite similar at different monomer concentrations and close to those found with benzene and in bulk. This supports the hypothesis of a similar scate of the propagating species, in contrast to the effect of methylene chloride. In summary, solvation by the polymer chain itself appears to predominate even in diglyme solutions. Methylene chloride on the other hand exerts a strong influence apparently disrupting the solvation by the polymer chains themselves.
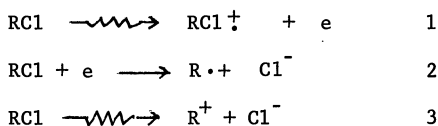
The molecular weights were also determined, in concert with the rate studies. These are difficult to interpret since in addition to being influenced by the propagation and other rate constants they are subject to chain transfer to monomer and solvents and to radiation degradation. In spite of these complications they did follow the rate data in a general sense.

RADIATION INDUCED IONIC GRAFTING

The extensive literature on radiation grafting is almost entirely concerned with free radical processes. It became clear, once radiation induced ionic polymerization was established, that ionic grafting would also be possible. The first successful attempts were apparently made by Jendrychowska-Bonamour (19) in 1968 with isobutylene grafted to polyvinyl chloride in the glassy state at low temperatures. The yields however were low and the doses high. The author and his colleagues had also made a few desultory attempts to graft isobutyl and ethyl vinyl ethers to PVC at about the same period at room temperature, again with rather poor yields. The formidable task of super drying both the monomers and the polymers was discouraging, to say the least. Later V. Ya Kabanov and his colleagues (20-22) initiated an extensive program of ionic grafting of several monomers to a number of polymeric substrates, including polyolefins. The work up to 1975 has been well summarized by Chapiro (23). Very recently Kabanov et al. (24) have published an interesting account of the effect of solvents on radiation induced ionic grafting. Some correlation of the yields with the donicity of the solvents used was demonstrated. Electron donor solvents tended to promote anionic and electron acceptor cation grafting. In both cases pure monomer appeared to be the most effective.

The author and his coworkers have reported the grafting of ethyl vinyl ether to polyvinyl chloride (25) and to polypropylene (26). The grafting-dose curves in the case of polyvinyl chloride powder are presented in Fig. 6. The effect of superdrying is quite dramatic, illustrating the ionic nature of the process. Interestingly, the wet monomer also grafted at similar rates to the dry and superdry systems but with a considerable induction period. This is in contrast to the polymerization of the pure monomer where the rates are greatly reduced by water but with no induction period. It would appear that in the presence of the polyvinyl chloride the water is actually consumed and not regenerated as with pure monomers.

The mechanism of cationic grafting onto polyvinyl chloride has been discussed by Chapiro (23). He suggested the following processes:

$$RCl \xrightarrow{\quad\rotatebox{0}{\leadsto}\quad} RCl\overset{\cdot}{+} \; + \; e \qquad\qquad 1$$

$$RCl + e \longrightarrow R\cdot + \; Cl^- \qquad\qquad 2$$

$$RCl \xrightarrow{\quad\rotatebox{0}{\leadsto}\quad} R^+ + Cl^- \qquad\qquad 3$$

Chapiro has suggested that Cl^- stabilizes the negative charges which reduces charge recombination and allows the cationic grafting reaction to proceed. We have shown with ESR and the irradiation of PVC dissolved in 2-methyltetrahydrofuran glass that the electron capture reaction does indeed take place (27). It is not clear how the water molecules are consumed in the grafting reaction. It is possible that water solvates the Cl^- ions essentially removing it from its normal inhibiting effect. In the case of polypropylene, water totally prevented any measurable degree of grafting, the conversion curves however showed no induction period whatever in contrast to the polyvinyl chloride results. This indicates that the presence of the PVC does appear to lead to the loss of the inhibiting effect of water during irradiation. This effect is presently being studied in more detail in these laboratories.

At the présent time the comparatively poor yields, even with elaborate and rigorous drying procedures, does not make radiation induced grafting too promising from an industrial standpoint. The doses required are rather high and there is considerable homopolymer formed. Some experiments are necessary with dry systems and high dose rates, using an electron accelerator, where ionic processes would be favored. Such experiments are experimentally difficult but will be made in the near future.

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