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The Radiation-Induced Cationic Polymerization of p-Methoxystyrene in Bulk and in Methylene Chloride Solution

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SUMMARY

The radiation-induced polymerization of p-methoxystyrene has been investigated in bulk and in methylene chloride solution under "super dry" conditions. The dose-rate dependence of the rate of polymerization was found close to 0.5 in both cases. At 20°C, the bulk polymerization rate constant is equal to 3.10^{-6} $\ell.\text{mole}^{-1}.\text{s}^{-1}$. The apparent activation energy of the polymerization is close to zero in pure monomer and in $CH_2C\ell_2$. The data are discussed and compared with independent results reported in the literature.

INTRODUCTION

The radiation-induced polymerization of a number of monomers is known to proceed through a free cationic mechanism under extremely dry conditions. (17,18)

A general kinetic scheme of these ionic reactions was first developed by Williams, Hayashi and Okamura(17,18) and an evaluation of the absolute propagation rate constant of the bulk polymerization of cyclopentadiene, styrene, α-methyl styrene and vinyl ethers has been reported. (1,3,5,6,10,14,16,17,18)

In more recent studies this scheme has been applied successfully to the radiation-induced polymerization of the vinyl ethers in solution. (7,8,15)

In the absence of impurities, mainly achieved by "superdrying" techniques the kinetics are expressed by equation (1).

$$R_p = \frac{k_p\,[M]\,R_i^{\,1/2}}{k_t^{\,1/2}} \qquad (1)$$

where R_p is the rate of polymerization, (M) the monomer concentration, R_i the rate of initiation, k_p and k_t are the rate constants for propagation and termination respectively. In this study we report the radiation-induced polymerization of p-methoxystyrene, performed under super-dried conditions, in bulk and in methylene chloride solution. These data are compared with independent results reported in the literature, using stable carbenium ion salts as initiators.

EXPERIMENTAL

Materials

p-Methoxystyrene was prepared from anisaldehyde through a Gignard synthesis (13) followed by the thermal dehydration of the corresponding alcohol. The monomer was then refluxed over calcium hydride and distilled under vacuum. The middle fraction was collected and dried under high vacuum over calcium hydride several sodium mirrors and finally barium oxide (10). Methylene chloride was treated with sulfuric acid, washed, dried over calcium chloride and distilled. The solvent was then sealed under vacuum and carefully dried over calcium hydride and sodium mirrors. The reagents were then stored in the dark at low temperature in ampoules fitted with breakseals.

Polymerization

The manifold of polymerization tubes was previously degassed under high vacuum, 10^{-5} torr at 480°C for 24 hours. Suitable amounts of monomer and solvent were then measured in a calibrated tube and transferred through breakseals and rotoflo grease-free stopcocks into the reaction ampoule. Samples remained frozen until they were irradiated. Irradiation was carried out in a cobalt-60 γ-ray source. Dose rates were determined through Fricke dosimetry. After the appropriate irradiation time the tubes were immediately opened and the polymer was precipitated in methanol. Polymer yields were determined gravimetrically.

RESULTS AND DISCUSSION

The radiation-induced polymerization of p-methoxystyrene was examined in bulk and in methylene chloride solution.

In order to determine the influence of any concurrent thermal polymerization of the monomer during the handling and the irradiation of the samples, some experiments were made under the same conditions but without irradiation. The extent of the thermal process was estimated to be considerably less than 10% of the ionic reaction and was neglected in the calculations.

The dose-rate dependence of the rate of polymerization was found to be close to 0.5 in both bulk and solution polymerizations as shown in Figure 1, indicating the absence of noticeable protonic impurities and thus permitting the application of the simple kinetic scheme described by equation 1.

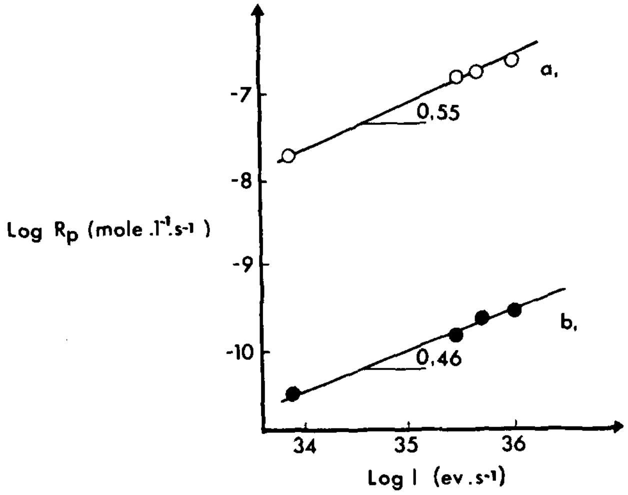

Figure 1. Dose-rate dependence of the rate of the radiation-induced polymerization of the p-methoxystyrene at 22^{0}C.

o bulk polymerization, a.

• polymerization in methylene chloride solution, b.

$[M]_0 = 3.3\ M \cdot L^{-1}$

The important decrease in the apparent rate of polymerization observed between the bulk and the methylene chloride solutions led us to examine the influence of the monomer concentration on the apparent rate of polymerization. The results are reported in Table I.

TABLE I

Influence of the monomer concentration on the rate of the radiation-induced polymerization of p-methoxystyrene, $CH_2C\ell_2$.I=4.4 X 10^{15} e.v./sec. T = 0°C

$[M]_0$ mole. L^{-1}	Irrad. Time min.	conversion %	$10^4.R_p$ mole. L^{-1} sec^{-1}
7.43 (Bulk)	2	2.07	12.80
6.83	5	3.52	8.01
5.94	15	4.64	3.06
4.03	37	5.87	1.06
3.35	35	4.55	0.72
1.56	80	7.76	0.25

A first order dependence would be expected from equation 1. between the rate and the monomer concentration. As shown in Figure 2 this simple dependence was not observed. This could be

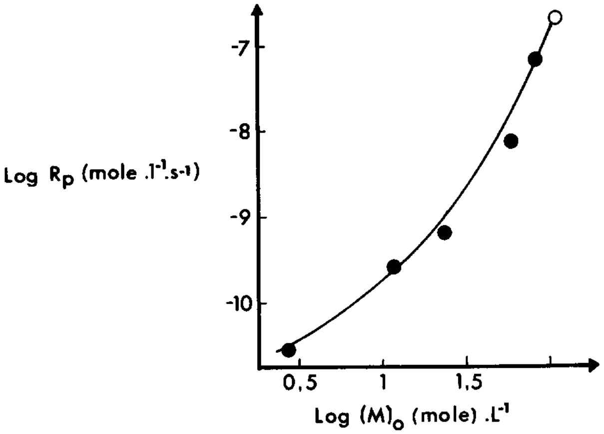

Figure II Monomer concentration dependence of the rate of the radiation-induced polymerization of p-methoxy styrene at 0^oC, dose rate: $4.4.10^{15}$ e.v./sec.

due to the substantial changes in the physical properties of the solution, such as the dielectric constant, which are not taken into account in this equation. Similar decreases of the activities in cationic polymerization of vinyl ethers (7,10,15) and oxiranes (11) when the overall dielectric constant of the reaction medium, ε, is increased, have been reported. This important effect of dielectric constant on the rate constant for reactions between an ion and a neutral molecule has been discussed in detail by Laidler and Eyring (9) who predicted a linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant, ε. Such a dependence is observed in the case of the p-methoxystyrene polymerization when plotting the logarithm of $R_p/[M]$ versus $\frac{1}{\varepsilon}$, as shown in Figure 3.

From the experimental rate of polymerization and a knowledge of R_i and k_t the polymerization rate constant k_p can be calculated.

Although the actual values of R_i and k_t are unknown for the p-methoxystyrene, those of both styrene and α-methyl styrene bulk polymerization are avaliable.(17,18)Very similar values have been reported for these parameters for both of the monomers and similar values for the p-methoxystyrene bulk polymerization was therefore assumed. This gives a rate constant, equal to 3.10^6 ℓ. mole.$^{-1}$ sec^{-1}, which is very close to the values reported for styrene and α-methyl-styrene, as indicated in Table II.

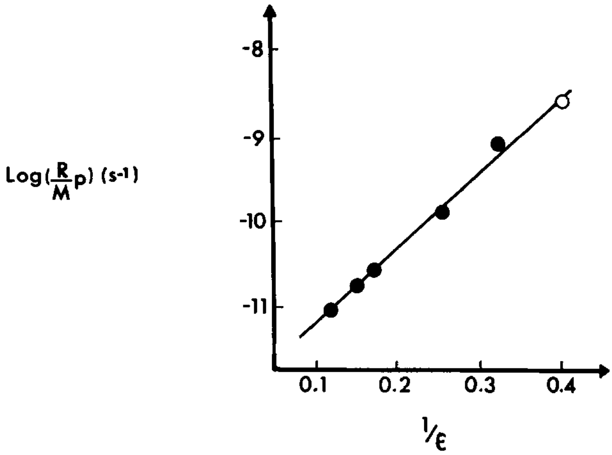

Figure III. Relationship between Ln. $R_p/[M]$ and 1/ε for the radiation induced polymerization of p methoxystyrene at 0°C, dose rate = $4.4.10^{15}$ e.v./sec.

TABLE II

Estimated rate constants of the bulk radiation-induced polymerization of styrene derivatives

Monomer	$k_p \times 10^{-6}$ $L.M^{-1}.sec^{-1}$	reference
cyclopentadiene	600 (-78°C)	(1,18)
styrene	3.5 (15°C)	(5,18)
α-methyl-styrene	3.4 (0°C)	(18)
p-methoxystyrene	3 (0°C)	this work

The value of k_p for the solution polymerization could not be estimated because of the lack of information on the R_i of mixtures of the monomer with methylene chloride which could introduce a large error into the data.

The activation energies were determined for the polymerization in bulk and in methylene chloride solution. The dependences of the logarithm R_p on the reciprocal of the absolute temperature are shown in Figure 4. The results are given in Table III.

TABLE III

Activation energies for the cationic polymerization of styrene derivatives

Monomer	catalyst	solvent	E_a Kcal.mole^{-1}	reference
cyclopentadiene	radiation	bulk	<2	1,17
cyclopentadiene	$Ph_3C^+SbCl_6^-$	CH_2C_2	-8	12
styrene	radiation	bulk	~ 0	18
α methyl styrene	radiation	bulk	~ 0	18
p methoxystyrene	radiation	bulk	~ 0	this work
p methoxystyrene	radiation	$CH_2C\ell_2$	~ 0	this work
p methoxystyrene	$Ph_3C+SbC\ell_6-$	$CH_2C\ell_2$	-5.6	2
p methoxystyrene	$C_7H_7^+SbC\ell_6-$	$CH_2C\ell_2$	+4.8	4

Some previous data concerning the bulk radiation-induced polymerization of cyclopentadiene, styrene, and α-methyl-styrene and of the cationic chemically-induced polymerization of cyclopentadiene and p-methoxystyrene in methylene chloride have also been included in the table.

The low activation energies, close to zero, observed for both the bulk and solution polymerization of p-methoxystyrene are in good agreement with the values found for the radiation-induced polymerization of styrene and α methyl styrene.

On the contrary the activation energies reported for the cationic polymerization of p-methoxystyrene initiated by carbonium ions (2,4) are quite different and even apparently in contradiction. A similar phenomenum is also observed between the radiation(1) and chemically(12) induced polymerization of cyclopentadiene. Several differences between these two types of initiating processes, as well as in the experimental conditions used can, in principle, explain these discrepencies.

Radiation-induced polymerizations proceed exclusively by a free ionic mechanism while chemically induced ones proceed through both ion-pairs and free ions. The equilibrium between these species depends on the temperature (2), in addition each species has its reactivity. A shift with the temperature in their relative proportion will therefore affect the rate of polymerization and consequently the apparent activation energy.

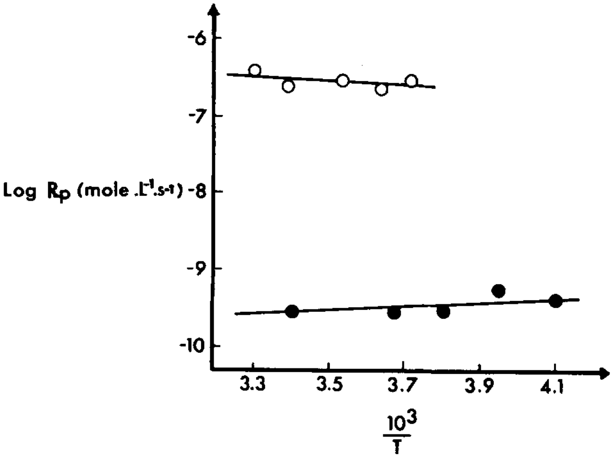

Figure IV. Arrhenius plot for the radiation-induced polymerization of p-methoxystyrene, I = $4{,}4.10^{15}$ ev/sec
o bulk polymerization
● polymerization in methylene chloride solution $[M]_0 = 3.3$ M.L^{-1}

Moreover during some of the chemical process, i.e., the polymerization initiated by trityl salts, some unreacted initiator remains in the reacting system. The important amount of this highly dissociated salt as well as the variation of its amount with the temperature can also affect drastically the ionic equilibrium of the propagating species. The negative activation energy observed in the trityl salt system and the opposite one reported by Goka and Sherrington (4) in the polymerization of p-methoxystyrene initiated by the cycloheptatrienyl cation where the initiation step can be expected to be complete, could be a reflection of these effects.

Another explanation for the observed negative activation energy has been proposed by Sigwalt et al (2) and concerns the existence of a solvation equilibrium between the active centers and the monomer. The high monomer concentration used in our study (3.3 M/L, about 100 times higher than the chemical polymerization) should then keep the equilibrium displaced towards the solvated species, while at lower concentrations, the ratio of solvated and non-solvated species should be greatly affected by the temperature. However in this case a discrepancy still remains between the two reported studies of the chemically-induced polymerization (2,4).

It is not possible at this time to decide between all these possible explanations and further investigations are sorely needed both in the chemical and the radiation cationic polymerization of p-methoxystyrene.

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