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The Polymerization of Acenaphthylene by Sulphuric Acid in Methylenedichloride

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SUMMARY

Acenaphthylene was polymerized in methylenedichloride at 273, 291 and 308 K by sulphuric acid. The initiation step takes place by addition of the proton of sulphuric acid to the monomer. The propagation step is through ion-pairs, and the propagation constants are first-order with respect to the monomer and initiator(k_p=0.22 $M^{-1}.s^{-1}$(273K), k_p=0.88 $M^{-1}.s^{-1}$(291K), k_p= 2.81 $M^{-1}.s^{-1}$(308K)). There is not appreciable loss of active centres, being this confirmed by experiments carried out with succesive additions of monomer. The molecular weights obtained confirm the importance of processes to monomer in this polymerization.

INTRODUCTION

Notwithstanding the numerous attempts carried out about the cationic polymerization of acenaphthylene(COHEN et al.1973) (GIUSTI et al.1966), (GIUSTI et al.1971), (PASK et al.1981), (PROSSER and YOUNG 1975), there are a few data existent about the values of the propagation constant, most of them referred to the initiation process.

Recently (PASK et al.1981) acenaphthylene polymerization in nitrobenzene using carbocation salts as initiators has been studied, the propagation constant value for unpaired cations has been obtained and some of the kinetic and spectroscopic complexities which can occur towards the end of the polymerization have been explained. However, as it is the only work in which direct data about the propagation step are obtained, we considered it would be interesting to study this polymerization in methylenedichloride using sulphuric acid as initiator.

EXPERIMENTAL

Materials

Acenaphthylene(Fluka purum) was purified according to the method of Flowers and Miller(FLOWERS and MILLER 1961) and the crystals of m.p. 92.5-93°C are obtained after two recrystallizations from methanol under dry N_2 atmosphere, dried in a high vacuum line and stored in the dark. Methylenedichloride was stirred with concentrated H_2SO_4 for several days, washed with water and dilute alkali, and dried with CaH_2. After distilling it was stored over fresh CaH_2 in a vacuum line. The initiator, sulphuric acid(Merck pro analysi) 98% was used without any further purification.

Kinetic procedure

Overall rates of polymerization were measured in a nitrogen-blanketted adiabatic calorimeter fitted with a Chromel-Alumel(Sodern) termocouple and a magnetic stirrer. Polymerizations were carried out under dry N_2(high quality); an initiator solution was placed in the reaction vessel and long phials of monomer solutions, capped under dry N_2, were introduced through the top of the flask; changes on thermocouple voltage were registered on a (Servograph Rec 16) recorder. Polymerization solutions were quenched by the addition of methanol. In some cases, once the reaction was completed, a successive polymerization experiment was carried out, by introducing a new monomer solution into the polymerization mixture from a long phial placed in the calorimeter. Spectrophotometric studies from reaction solutions were conducted using a Bechman 5200 spectrophotometer following standard techniques. Molecular weights of polyacenaphthylene samples were measured on a Waters Permeation Chromatograph(G.P.C)(model 6000 A) using tetrahydrofuran solutions at 25°C. The G.P.C. columns(microstyragel 10^2, 5.10^2 and 10^4 Å), were calibrated from the universal calibration equation obtained with narrow polystyrenes perfectly characterized and the intrinsic viscosities data for samples of polyacenaphthylene in tetrahydrofuran at 25°C(LANDABIDEA 1978).

RESULTS AND DISCUSSION

In all experiments carried out total conversion is achieved. A plot of $\ln(|M|_0/|M|)$ vs. time is given in Figure 1. As it can be seen, after the induction period, in which in the average 40% of the monomer is consumed, a linear dependence is observed; this result being indicative that the initiation step is slow and the propagation reaction is first-order with respect to the monomer.However, from detailed study of this plot it can be confirmed that initially there is a zone where a small portion of monomer($\simeq$7%) is consumed very quickly and, afterwards the induction period takes place.

This initial jump was systematically obtained and no dependence on initial monomer or initiator concentrations has been observed being, however, a function of the temperature. Therefore, it must be related to the kind of initiator. In our reactions, sulphuric acid can be present in the organic phase and in aqueous phase and its concentrations in both phases is given by the equilibrium constant; the concentration in the organic phase will be very small(HAYES and PEPPER 1961) and the initial jump observed can be due to the reaction of sulphuric acid present in this phase with the monomer, this reaction is very fast. As the sulphuric acid in the organic phase disappears the equilibrium is broken, and the sulphuric acid in aqueous phase passes towards the organic phase. If this process were relatively slow, the effect in the reaction would have been to accrue progressively the number of active centres capable of polymerization. All this would correspond to the induction period observed in every reaction. This period would finish when all the sulphuric acid would have gone to the organic phase and reacted with the monomer. From this moment, all possible active centres would have been created and the reaction would be in the propagation step.

Preliminary experiments showed that when sulphuric acid was present only in the organic phase, the induction period did not takes place, the reaction having initially a very fast conversion of monomer("initial reaction"), followed by the propagation reaction at a lower rate. This behaviour is characteristic in the initiation step in many cationic polymerizations of acenaphthylene(COHEN et al.1973), (GIUSTI et al.1966), (GIUSTI et al.1971), (PASK et al.1981) and it is in accordance with the observations made during our reactions.

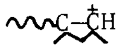
Moreover, after the induction period is finished a stationary period is reached in which there is no apparent upper limit in the conversion; this fact is indicative that the initiation is quantitative and that there is no appreciable loss of active centres. This is confirmed with experiments carried out with successive additions of monomer. In Figure 2 one of these experiments can be observed. As it can be seen, there is neither initial jump nor induction period, showing that the active centres were already created and that the initiation was quantitative. The fact that in the first and in the second reaction the kinetic order is maintained up to the final, as well as the fact that the pseudoconstant values are alike, show that obviously there is not appreciable loss of active centres.

The propagation constant, k_p, has been obtained as the ratio of the first order pseudoconstant to the initial concentration of sulphuric acid. The k_p values at 273, 291 and 308K are summarized in Tables 1-3. The mean values obtained at these temperatures are: At 273K, $k_p=0.22\ M^{-1}s^{-1}$; at 291K, $k_p=0.88\ M^{-1}s^{-1}$; at 308K, $k_p=2.81\ M^{-1}s^{-1}$.

TABLE 1.- k_p values at 273K

Exp.	$\|M\|_o$ $(mol.l^{-1})$	$\|I\|_o$ $(mol.l^{-1})$	k_p $(l.mol^{-1}.s^{-1})$
AO-3	0.10	0.10	0.17
AO-4	0.15	0.10	0.37
AO-5	0.15	0.12	0.15
AO-6	0.18	0.06	0.15
AO-7	0.20	0.08	0.22
AO-8	0.20	0.10	0.26
AO-10	0.20	0.05	0.37
AO-11	0.30	0.04	0.15
AO-12	0.30	0.10	0.21
AO-13	0.30	0.05	0.18

Even through the temperature range was narrow and the number of experiments made at 308K was small, it is possible to obtain an estimative value for the activation energy of 12.2 kcal.mol^{-1}, in agreement with the one reported by Imoto(IMOTO and TAKEMOTO 1955) for a propagation through the cation



This species was also proposed by other authors(COHEN et al. 1973), (GIUSTI et al.1966), (GIUSTI et al.1971),(PASK et al. 1981), (PROSSER and YOUNG 1975),(HAYES and PEPPER 1961).

TABLE 2.- k_p values at 291K

Exp.	$\|M\|_o$ (mol.l^{-1})	$\|I\|_o$ (mol.l^{-1})	k_p (l.mol^{-1}.s^{-1})
BO-1	0.10	0.05	1.23
BO-3	0.10	0.05	0.67
BO-4	0.11	0.05	1.09
BO-6	0.11	0.06	0.91
BO-7	0.11	0.10	0.83
BO-9	0.15	0.06	0.85
BO-10	0.15	0.10	0.75
BO-12	0.15	0.10	0.73
BO-17	0.20	0.03	0.69
BO-18	0.20	0.04	1.07
BO-19	0.20	0.05	1.17
BO-21	0.20	0.08	1.10
BO-22	0.21	0.06	0.86
BO-24	0.21	0.10	1.10
BO-26	0.21	0.10	0.68
BO-28	0.30	0.10	0.78
BO-30	0.30	0.05	0.91
BO-32	0.30	0.10	0.96
BO-33	0.15	0.10	0.88

TABLE 3.- k_p values at 308K

Exp.	$\|M\|_o$ (mol.l^{-1})	$\|I\|_o$ (mol.l^{-1})	k_p (l.mol^{-1}.s^{-1})
CO-1	0.18	0.06	2.95
CO-2	0.18	0.10	2.44
CO-4	0.18	0.12	2.95
CO-5	0.18	0.15	2.90

The k_p value at 291K is lower the one given for propagation through free ions (k_p=23.32 M^{-1}.s^{-1})(PASK et al.1981). This is an indication that in our system the propagation is through ion-pairs, which is reasonable taking into account the characteristic of the solutions of sulphuric acid in similar solvents(HAYES and PEPPER 1961).

Molecular weight studies showed that unimodal distributions were obtained in all experiments. Moreover, no significative dependence has been found between the molecular weight and either monomer or initiator concentration.

In our opinion this dependence is consequence of the important transfer processes to the monomer. the approximate molecular weight was of 4000 and its polidispersity of 1.7.

Besides, the fact that in reactions with successive monomer additions the molecular weughts were unaffected with respect to that obtained with only one addition, can be explained in a similar way as a consequence of the transfer processes, these processes being in open competition with propagation processes.

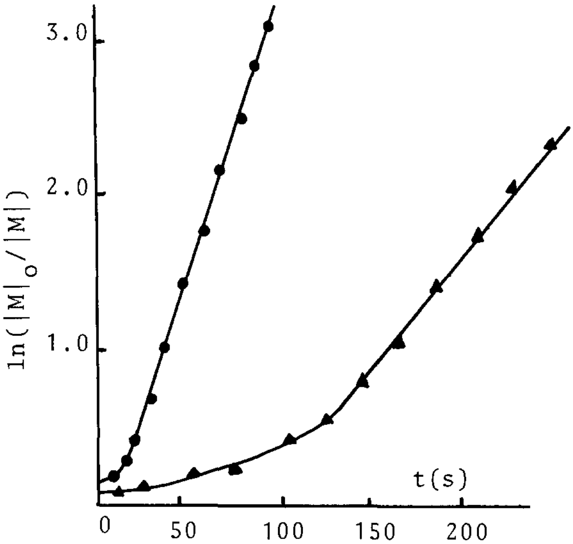


Figure 1.- First order plots.
(▲-Exp.(AO-12); ●-Exp.(BO-32)

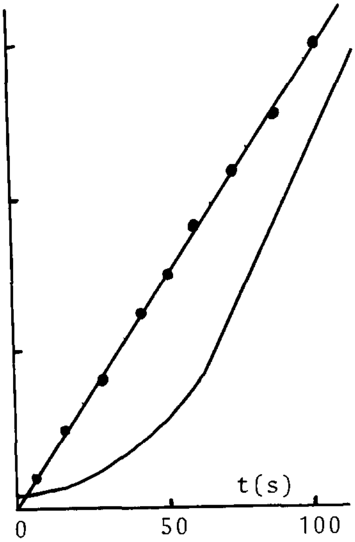


Figure 2.-First order plots.(●-after a new addition.

The constancy of molecular weights after second addition of monomer is not a peculiar distinction of this system, but it has also been reported for the polymerization of acenaphthylene with $TiCl_4$-CCl_3CO_2H as initiator (PROSSER and YOUNG 1975).

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