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Photopolymerization of unsaturated cyclic ethers

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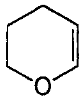
2,3-Dihydro-4H-pyran, DHP, and 2,3-dihydrofuran, DHF, are photopolymerized at ambient temperature with the aid of diphenyl iodonium hexafluorophosphate, $Ph_2I^+PF_6^-$ or triphenyl sulfonium hexafluorophosphate, $Ph_3S^+PF_6^-$ at $\lambda_{inc} = 310$ or 340 nm, respectively. DHP is photopolymerized in bulk with the aid of $Ph_2I^+PF_6^-$ and in CH_2Cl_2 solution with the aid of $Ph_3S^+PF_6^-$. The average molar mass of the polymer is low and the propagation involves both $C = C$ bonds and ring-opening. DHF is photopolymerized in CH_2Cl_2 solution using $Ph_3S^+PF_6^-$. The average molar mass of the polymer increases with conversion (living polymerization) and can become high (4×10^5 g mol^{-1}). The propagation exclusively involves $C = C$ bonds. Dark polymerization of DHF occurs at ambient temperature upon the addition of $Ph_2I^+PF_6^-$, but $Ph_3S^+PF_6^-$ is inert against DHF. DHP does not undergo dark reactions with the two salts. © 1997 Elsevier Science Ltd.

(Keywords: photopolymerization; cationic polymerization; 2,3-dihydro-4H-pyran)

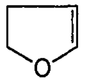
INTRODUCTION

This paper reports on the cationic photopolymerization of heterocyclic compounds of the structure



DHP

2,3-dihydro-4H-pyran

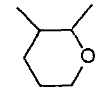


DHF

2,3-dihydrofuran

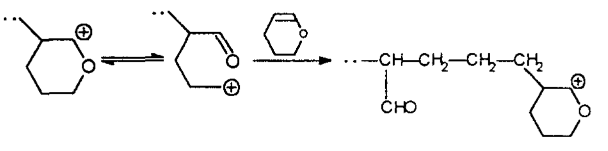
using certain onium salts as photoinitiators. Actually, photoinitiated cationic polymerizations using onium salt type initiators have attracted the interest of many researchers during the last years and in this way several technically applicable processes were developed[1-6]. Notably, the former work concentrated on oxirane type compounds (epoxides), vinyl ethers of the structure $CH_2 = CH_2$–OR and to some extent on tetrahydrofuran. To the best knowledge of the authors of this paper the photopolymerization of unsaturated cyclic ethers such as DHP and DHF was not investigated so far.

The polymerization of DHP[7,8] and DHF[9-14] in the dark was studied in the past and the results of that work shall be briefly reviewed here:(a) DHP was shown to polymerize via a cationic mechanism with the aid of Friedel–Crafts initiators such as BF_3-etherate in dilute solution (solvents: petrol ether, toluene) at 0 and 20°C[7,8] and to exhibit essentially vinyl ether-like behaviour, i.e. the polymerization proceeds predominantly *via* carbon–carbon double bonds leading to long segments containing moieties of structure **I**,

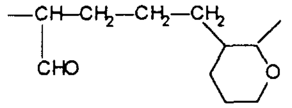


I

However, the polymeric product contains aldehyde groups indicating that the propagation also involves ring opening reactions as is illustrated by reaction (1)[7]:



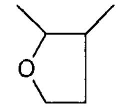
In this way segments containing structure **II** are formed.



II

Polymers of softening temperatures ranging from 170 to 200°C are obtained in this way. Moreover, the spontaneous cationic polymerization of CT-complexes containing DHP, the latter functioning as electron donor, was reported[15]. Notably, the cationic polymerization of 2,3-dihydro-4H-pyran derivatives has become of some interest regarding the synthesis of biodegradable polymers[16,17].

(b) 2,3-Dihydrofuran and methyl-substituted 2,3-dihydrofurans were reported[9] to be converted with the aid of BF_3 at −80°C to polymers of high molar mass (on the basis of intrinsic viscosity measurements) and high softening temperatures (118°C, poly(2,3-dihydrofuran); 245°C, poly(2,3-dihydro-5-methylfuran)). From the infra-red (i.r.) spectra recorded with poly(2,3-dihydrofuran) it was concluded that the polymer consists of moieties corresponding to structure **III**.



III

Therefore, the propagation is thought to proceed *via* carbon–carbon double bonds, rather than via ring opening. Interestingly, also the living cationic polymerization was achieved[13], in the case of DHF at −40°C with the aid of

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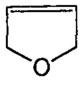
iodine in toluene or dichloromethane solution, and in the case of 5-methyl-2,3-dihydrofuran at −78°C with the aid of acetyl perchlorate in toluene solution.

Notably, 2,5-dihydrofuran does not polymerize under any conditions [9].



2.5–dihvdrofuran

EXPERIMENTAL

Materials

Onium salts. $Ph_3S^+PF_6^-$ was synthesized from triphenyl sulfonium bromide and sodium hexafluorophosphate according to a prescription of Dektar and Hacker[18]. The salt was recrystallized from ethanol. $Ph_3S^+Br^-$ was prepared by a Grignard reaction from bromobenzene and diphenylsulfoxide. $Ph_2I^+PF_6^-$ was prepared as described by Crivello and Lam[19]. It was recrystallized prior to use from water. The onium salts under investigation are known to form protonic acid upon standing, a process promoted by traces of water. Therefore, care was taken to keep the acid content as low as possible by repeated recrystallization. The protonic acid content was controlled by potentiometric determinations of the proton concentation in solutions of the salts (solvent: acetonitrile/water (3/7, v/v) with the aid of a glass electrode (Ingold 405-S7).

Monomers. 2,3-Dihydro-4H-pyran (DHP) was obtained from Acros Chimica (99%). It was refluxed with anhydrous sodium carbonate and distilled under argon. The fraction boiling at 85–86°C was refluxed over sodium wire overnight and distilled again. 2,3-Dihydrofuran (DHF) was obtained from Acros Chimica (97%). It was refluxed with KOH overnight and distilled under argon. The fraction boiling at 54–55°C was refluxed with sodium wire and distilled again.

Solvent. Dichloromethane (Merck) was dried with CaH_2 and distilled. It was stored over molecular sieve (0.4 nm, Merck).

Proton scavenger. 2,6-Di-*tert*-butyl-4-methyl pyridine (DBMP) was purchased from Aldrich and used as received.

Polymerization

All experiments were carried out under argon at room temperature (*ca* 22°C). If possible experiments were performed with solvent-free monomer and the onium salt was dissolved in the monomer prior to irradiation. When the onium salt did not dissolve in the neat monomer dichloromethane was added to improve the solubility. The onium salt concentrations varied from 3×10^{-3} to 5×10^{-3} mol dm^{-3}.

For irradiations a xenon lamp (Osram, XBO 450 W) operated in conjunction with a monochromator (Polytech, model GM 252) was used. The conversion of monomer was determined by measuring the area under the monomer peak in size exclusion chromatograms recorded with the reaction mixture.

Characterization of polymers

Size exclusion chromatograms of the polymer samples were recorded with a set of Ultrastyragel columns (Waters, 500, 10^3, 10^4, 10^5 Å) using THF as eluent. Moreover, M_w, the weight average molar mass was determined by the light scattering (LS) method in tetrahydrofuran solution at 22°C: $dn/dc = 0.118$ ml g^{-1} (PDHP) and $dn/dc = 0.112$ ml g^{-1} (PDHF).

RESULTS

Dark reactions

2,3-Dihydropyran. $Ph_2I^+PF_6^-$ is soluble, but $Ph_3S^+PF_6^-$ is insoluble in DHP. $Ph_2I^+PF_6^-$ is inert toward DHP for a period of up to 3 days. After this time a small fraction of the monomer is converted to polymer which is probably due to a small quantity of protonic acid contained in the salt as impurity. $Ph_3S^+PF_6^-$ is soluble in a mixture of DHP and dichloromethane (6/4, w/w) and does not undergo a dark reaction with DHP within 3 days.

2,3-Dihydrofuran. $Ph_2I^+PF_6^-$ is soluble, but $Ph_3S^+PF_6^-$ is insoluble in DHF. The latter salt is soluble in a mixture of DHF and dichloromethane (6/4, w/w). $Ph_2I^+PF_6^-$ initiates the polymerization of DHF in a dark reaction and a polymer of rather high average molar mass is formed ($M_w \approx 10^5$ g mol^{-1}). The polymerization is quite exothermic and commences shortly after the dissolution of the onium salt. By contrast, $Ph_3S^+PF_6^-$ is inert toward DHF in the dark.

Photopolymerization of 2,3-dihydropyran

Bulk polymerization. Bulk DHP containing $Ph_2I^+PF_6^-$ was polymerized at room temperature upon irradiation at $\lambda = 340$ nm to high conversion as can be seen from *Figure 1*. When DBMP, a typical proton scavenger, was present in the reaction mixture (0.02 mol dm^{-3}), no polymer was formed during irradiation (20 h) indicating that protons act as initiators. The molar mass distribution of the polymer is rather broad and the average molar mass is rather low, but a small fraction of relatively high average molar mass ($M_w = 2 \times 10^5$ g mol^{-1}), determined by the LS method, was precipitated with methanol from a THF solution of the polymer. At a total monomer conversion of about 90% the high molecular fraction corresponded to only about 4%. From the i.r. absorption spectra recorded with both fractions it is concluded that C = C bonds are decomposed (decrease in the intensity of bands at 1639 cm^{-1} and 930 cm^{-1}) which implies that propagation *via* the carbon–carbon double bond occurs and that large polymer segments consisting of moieties of structure **I** are formed. The i.r. spectrum of the low molecular fraction also contains a sharp band at 1724 cm^{-1} indicating the existence of carbonyl groups. Additional

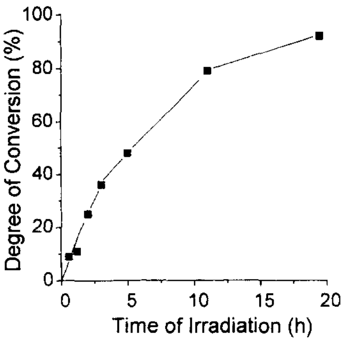


Figure 1 Bulk polymerization of DHP containing $Ph_2I^+PF_6^-$ (3×10^{-3} mol dm^{-3}) at 22°C and $\lambda = 340$ nm (OD = 0.22 at $d = 0.6$ cm). Degree of monomer conversion *versus* time of irradiation

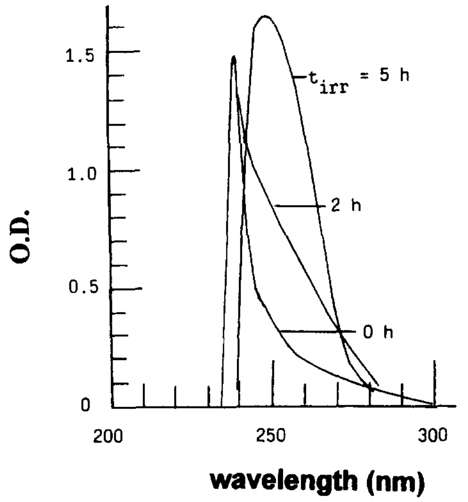


Figure 2 Bulk polymerization of DHP containing $Ph_2I^+PF_6^-$ (3×10^{-3} mol dm^{-3}) at 22°C and λ_{inc} = 340 nm (OD = 0.22 at d = 0.6 cm). Optical absorption spectra of the reaction mixture recorded after various times of irradiation. Prior to recording the reaction mixture was diluted with tetrahydrofuran at a ratio 1/100

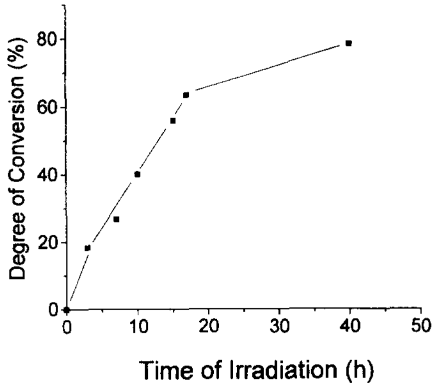


Figure 3 Polymerization of DHP containing dichloromethane (40 wt%) and $Ph_3S^+PF_6^-$ (5.0×10^{-3} mol dm^{-3}) at 22°C and at λ_{inc} = 310 nm (OD = 0.24 at d = 0.6 cm). Degree of monomer conversion *versus* time of irradiation

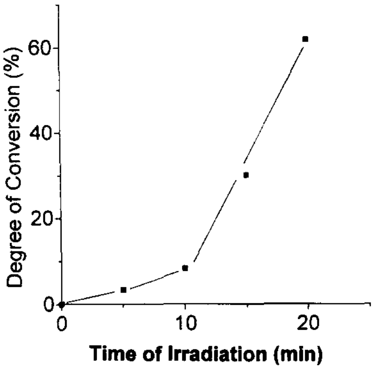


Figure 4 Polymerization of DHF containing dichloromethane (40 wt%) and $Ph_3S^+PF_6^-$ (3.4×10^{-3} mol dm^{-3}) at 22°C and at λ_{inc} = 310 nm (OD = 0.24 at d = 0.6 cm). Degree of monomer conversion *versus* time of irradiation

evidence for the formation of carbonyl groups comes from the change in the ultra-violet (u.v.) absorption spectrum during polymerization. As can be seen from *Figure 2* the absorption spectrum of the irradiated reaction mixture possesses a new band around 240–270 nm. It remains with the low molecular fraction and is thought to correspond to the carbonyl group (aldehyde group) generated by ring-opening processes leading to polymer moieties of structure **II**. In conclusion, the photopolymerization of DHP involves both propagation via C—C double bonds and ring-opening. In this connection it is noticeable, that quite analogous findings were obtained by Kamio *et al.*[7] upon initiating the cationic polymerization of DHP with the aid of BF_3-etherate.

Polymerization in solution. Also $Ph_3S^+PF_6^-$ is appropriate a photoiniator for the polymerization of DHP as can be seen from *Figure 3*. Because of the insolubility of the sulfonium salt in neat DHP the reaction mixture contained dichloromethane (40 wt.%) in this case. The rate of monomer conversion is low and similar to that observed in the case of neat DHP using $Ph_2I^+PF_6^-$ as initiator. It amounts to about 0.06%/min.

Photopolymerization of 2,3-dihydrofuran in solution

DHF containing dichloromethane (40 wt%) and $Ph_3S^+PF_6^-$ (3.4×10^{-3} mol dm^{-3}) was polymerized at 22°C upon irradiation at λ_{inc} = 310 nm to high conversion. As shown in *Figure 4* the monomer conversion commences after an induction period of several minutes and then proceeds with a rate of about 6% per minute, which is about 100 times higher than the rate of monomer conversion in the case of DHP. When DBMP was present in the reaction mixture (0.02 mol dm^{-3}) no polymer was formed during the irradiation (19 h) indicating that protons act as initiators. The weight average molar mass (determined by the LS method) of the polymer obtained at t_{irr} = 20 min is rather high, $M_w = 4 \times 10^5$ g mol^{-1}. Notably, features characteristic of a living polymerization process are recognizable in this case: M_w grows with increasing irradiation time. This can be seen from *Figure 5* where size exclusion chromatograms recorded with the reaction mixture after various irradiation times are shown. Obviously, the position of the polymer peak is shifted to lower elution volumes (corresponding to higher average molar masses) as the time of irradiation increases. This behaviour is typical of the occurrence of living polymerization. The analysis of the i.r. spectrum of the polymer revealed the following: the spectrum of the polymer does not possess bands at 703 cm^{-1} and 1607 cm^{-1} characteristic of C = C bonds contained in the spectrum of the monomer. On the other hand, the spectrum of the polymer contains a very strong band at 1065 cm^{-1} and a strong band at 923 cm^{-1} characteristic of C—O—C bonds. Notably, the absorption spectrum of the irradiated reaction mixture does not contain a new band between 240 and 270 nm due to carbonyl groups as in the case of DHP. This implies that the polymerization of DHF is based on propagation *via* the double bonds and not *via* ring-opening, i.e. the polymer consists of moieties of structure **III**. Obviously, both initiation by Friedel–Crafts initiators and photoinitiation with the aid of $Ph_3S^+PF_6^-$ leads to polymers of quite similar chemical structure.

It is also interesting to note that upon performing experiments at low temperature observations were made that are at variance with earlier findings concerning the BF_3-initiated polymerization of DHF[9] (*vide ante*). When the system $DHF/CH_2Cl_2/Ph_3S^+PF_6^-$ was irradiated at −78°C no polymer was formed during the irradiation. However, polymer was generated slowly when the irradiated solution was warmed up to room temperature.

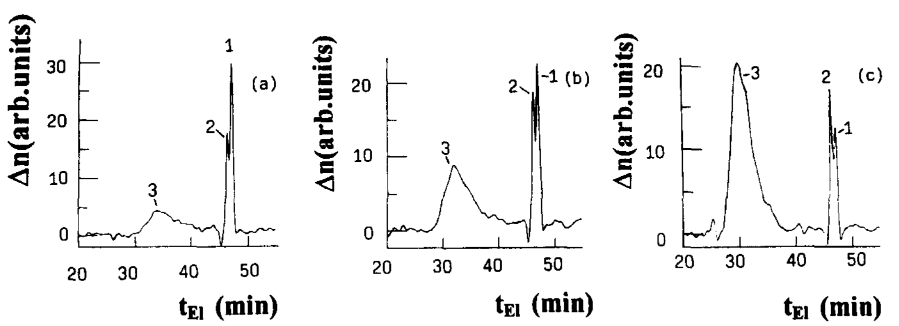
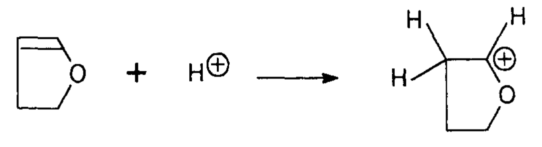


Figure 5 Polymerization of DHF containing dichloromethane (40 wt%) and $Ph_3S^+PF_6^-$ (3.4×10^{-3} mol dm^{-3}) at 22°C and at $\lambda_{inc} = 310$ nm (OD = 0.24 at $d = 0.6$ cm). Size exclusion chromatograms recorded with the reaction mixture after various times of irradiation 10 min (a), 15 min (b), 20 min (c). See *Figure 4* for corresponding conversion. Peak denotations: DHF monomer (1), CH_2Cl_2 (2), polymer (3)

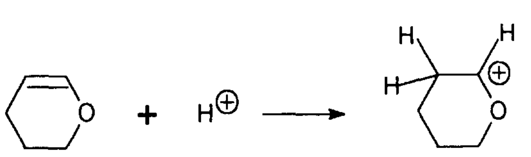
DISCUSSION

The results show that both $Ph_2I^+PF_6^-$ and $Ph_3S^+PF_6^-$ are photoinitiators for the cationic polymerization of DHP. In the case of DHF only $Ph_3S^+PF_6^-$ can be used as photoinitiator because $Ph_2I^+PF_6^-$ undergoes a quite effectively proceeding dark reaction with DHF thereby converting the monomer into a polymer of high molar mass. Provided electron transfer is the driving force for the dark reaction of onium ions with unsaturated cyclic ethers the onium ion possessing the higher (less negative) reduction potential should be more reactive. Accordingly, Ph_2I^+ ($E_{red} = -0.2$ V, SCE) should be more reactive than Ph_3S^+ ($E_{red} = -1.2$ V, SCE). In this way the differences in reactivity of the two onium ions towards DHF might be explained.

Regarding the photoinitiation mechanism the experiments with the proton scavenger DBMP revealed the important role played by protons, i.e. the results suggest that protons generated via the photolysis of onium ions react with DHF and DHP according to reactions (2) and (3), respectively.

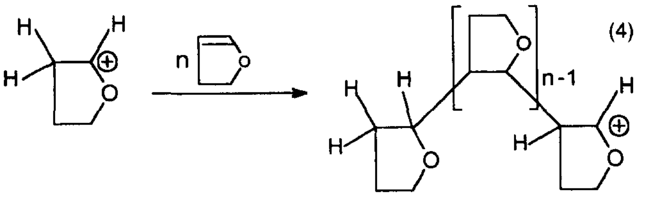


(2)



(3)

The carbocations generated in this way initiate the propagation as illustrated by reaction (4) for the case of the polymerization of DHF.



(4)

The question now arises why, under comparable experimental conditions, DHF is converted about 100 times faster than DHP. Actually, two factors concerning the initiation and the propagation might be considered here: (a) The attachment of protons to DHP according to reaction (3) is less effective than in the case of DHF according to reaction (2). This implies that in the case of DHF the stationary concentration of initiating species is higher than in the case of DHP. (b) The propagation rate constants differ by a large factor, i.e. $k_p(\mathrm{DHF}) \gg k_p(\mathrm{DHP})$. Whether and to what extent these factors apply here cannot be decided at present. Moreover, it appears that the two systems differ significantly as far as termination and chain transfer are concerned. The polymer formed from DHP possesses a much broader molar mass distribution and a much lower average molar mass than that generated from DHF. Notably, there are features indicative of living polymerization only in the case of DHF but not in the case of DHP. The polymeric product generated from DHP consists of two fractions. The larger one, being of low average molar mass, contains carbonyl groups, which indicates that ring-opening plays an important role in this case. On the other hand, no carbonyl groups are detectable in the polymer obtained from DHF indicating that ring-opening reactions are unimportant in this case and that propagation involves exclusively the reaction of carbon–carbon double bonds.

With respect to the early work referred to in the introduction section the apparent discrepancy between the BF_3-induced[9] and the light-induced polymerization of DHF is noticeable. Whereas the BF_3-induced polymerization of DHF leads to a polymer of high molar mass only at low temperature (– 80°C)[9], u.v. irradiation of the system DHF/ $CH_2Cl_2/Ph_3S^+PF_6^-$ at low temperature does not yield polymer at all. But polymer of high molar mass formes after photochemical initiation at ambient temperature.

CONCLUSIONS

The experiments described in this paper show that the cationic polymerization of the unsaturated cyclic ethers DHP and DHF can be initiated photochemically with the aid of appropriate onium salts. Moreover, the results reveal basic differences regarding the cationic polymerization of these two compounds: in the case of DHF the propagation process involves exclusively the reaction of carbon–carbon double bonds, and in the case of DHP in addition also the ring-opening reaction.

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