THERMAL CATIONIC POLMERIZATION OF TETRAHYDROFURAN INDUCED BY DIPHENYLIODONIUM SALT IN THE PRESENCE OF COMMON SOURCES OF FREE RADICALS.

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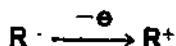(Received January 19 th, 1982)

SUMMARY

Bulk polymerization of tetrahydrofuran has been studied utilizing diphenyliodonium hexafluorophosphate in the presence of phenylazotriphenyl methane, benzoyl peroxide and 2—2'—azo—bis. isobutyro nitrile. The effects of the cationic salt and free radical initiator on the rate of polymerization have been investigated for all initiation systems.

INTRODUCTION

In recent years, there has been a growth of interest in the development of new initiators for cationic polymerization[1—3]. Aryl diazonium salts[3] (ArN$_2$$^+X^-$), diaryl iodonium salts[4] (Ar$_2$I$^+$X$^-$) and triaryl sulfonium salts (Ar$_3$S$^+$X$^-$) are especially useful as photochemical initiators for cationic polymerizations of epoxides, alkyl vinyl ethers and other related monomers. Only aryl diazonium salts are known to decompose thermally[6], although all three types of salt yield cationic species on u.v. irradiation at appropirate wavelength.

Recently, Ledwith and co—workers[7—9] have presented an evidence for the oxidation of election donor free radicals to corresponding carbocations;

$$R \cdot \xrightarrow{\;-e\;} R^+ \qquad\qquad 1$$

and experimental results for its application to polymerizing systems.

In continuation of these studies we now report the use of thermally decomposing free radical sources in cationic polymerization of tetrahydrofuran and mechanistic details are presented.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) (Merck) was purified by the conventional drying and distillation procedures. Phenylazotriphenyl methane[10] (PAT) and diphenyliodonium. hexafluorophosphate[11] were synthesized according to established procedures. Benzoyl peroxide (Fluka) was recrystallized from chloroform with addition of petroleum ether. 2,2'-azo-bis-isobutyranitrile (AIBN) (Fluka) was recrystallized from absolute ethanol as white crystals.

Polymerization procedure

Bulk monomer (THF) was directly distilled to the reaction vessel containing known amount of initiator and activator. The reaction vessel was vacuum sealed in the usual manner and stored in liquid nitrogen until used. The same procedure was followed for all samples. Initiation was effected by placing the vessels in an oil bath at 80°C for 10 minutes. Reaction mixtures were then immersed in a thermostated water bath at 40°C for usually 60 minutes during which time a dark colour developed. At the end of this time, polymer was obtained by precipitation into water containing little base. Conversions were calculated on the basis of 100% theoretical yield being 882,3 gms polytetrahydrofuran from 1 litre of monomer at 25°C.

Calculation of rates of Polymerization

The rates were determined gravimetrically from the following expression

$$R_p = \frac{W}{M} \times \frac{1000}{V} \times \frac{I}{t}$$

                                                                                2

where.

W = Weight of polymer produced (g)

M = Monomer moleculer weight (g/mol g)

V = Volume of solution in reaction vessel (ml)

t = Polymerization time (sec.)

Calculation of active centre concentration

The active centre concentralton, [C+], can be calculated from the simple kinetic expression

$$R_p = k_p \, [THF] \, [\text{Active Centres}]$$

                                                                                3

For our purposes, it seemed appropriate to use the value of k_p (6.4 . 10^{-3} M^{-1} sec^{-1} at 40°C) extrapolated from the data of Croucher and Wetton[12] who utilized p—Chlorophenyldiazonium hexafluorophosphate as initiator for the bulk polymerization of THF.
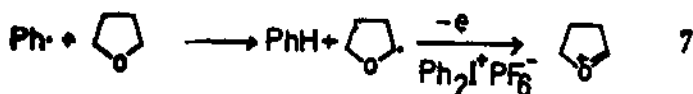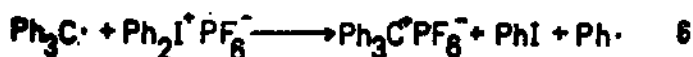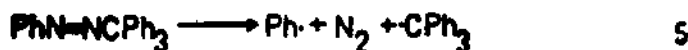
Molecular Weight Measurements

Number Avarage molecular weights were estimated from measurements of solution viscosity in benzene at 30°C with the aid of the relation[13]

$$(\eta) = 1.31 \times 10^{-4} M_n^{-0.9} \qquad\qquad 4$$

RESULTS AND DISCUSSION

Diphenyliodonium hexafluorophosphate was used as a cationic salt throughout the work. In the case of triphenylazophenyl methane as a radical source, possible reactions may be generalised as follows.

$$PhN=NCPh_3 \longrightarrow Ph\cdot + N_2 + \cdot CPh_3 \qquad\qquad 5$$

$$Ph_3C\cdot + Ph_2I^+PF_6^- \longrightarrow Ph_3C^+PF_6^- + PhI + Ph\cdot \qquad 6$$

$$Ph\cdot + \underset{O}{\bigcirc} \longrightarrow PhH + \underset{O}{\bigcirc}\cdot \xrightarrow[\ Ph_2I^+PF_6^-\ ]{-e} \underset{O}{\bigcirc} \qquad 7$$

The azo compound may be conviniently decomposed by heating to give triphenyl metyl radical (readily oxidised to the corresponding cation which is well known initiator for cationic polymerization[14]) and a phenyl radical which is also produced from fragmentation of the salt. (reactive in hydrogen abstraction).

Table I and II illustrate the dependence of the polymerization rate on the azo compound and iodonium salt respectively.

TABLE I.
POLYMERIZATION[a] OF THF (BULK)

$(Ph_2 I^+PF_6^-) = 5 \times 10^{-4} M$

PhN=NCPh₃ (M)	Conversion (%)	$R_n \cdot 10^4$ (M . sec.⁻¹)	$C^+ \times 10^4$ (M)
2×10^{-3}	6.35	2.16	2.80
4×10^{-3}	9.01	3.06	3.97
6×10^{-3}	10.85	3.68	4.78
8×10^{-3}	9.67	3.29	4.27
10^{-2}	10.40	3.53	4.59
1.4×10^{-2}	11.95	4.10	5.27

[a]Polymerizations were carried out by heating reaction mixtures at 80°C for 10 minutes and then standing at 40°C for 60 minutes.

TABLE II.
POLYMERIZATION* OF THF (BULK)
$(PhN=NCPh_3) = 5 \times 10^{-3}M$

$(Ph_2 I^+PF^-_6)$ (M)	Conversion (%)	$R_p . 10^4$ (M . sec.$^{-1}$)	$C^+ . 10^4$ (M)
2×10^{-3}	0.1	—	—
4×10^{-3}	4.96	1.69	2.19
5×10^{-3}	6.14	2.10	2.71
8×10^{-3}	13.10	4.45	5.77
10^{-2}	16.29	5.54	7.19

*Polymerizations were carried out as described in Table 1

Initiation at 80°C was chosen to allow production of active chains, but little growth. Rapid quenching to lower temperatures (40°C) then allows growth with simoultaneus initiation.

We have observed that the rate of polymerization increased with $(PhN=NCPh_3)$ until certain concentration is reached, and thereafter levelled off, even decreased at higher concentrations. Conversion to poly THF was found to increase linearly with iodonium salt concentration, whereas no increase was detected[15] at high concentrations of the salt when photochemical sources of free radicals employed.

The same behaviour was observed when benzoyl peroxide used as free radical source. The results are shown in Table III and Table IV.

TABLE III.
POLYMERIZATION* OF THF (BULK)
$(Ph_2 I^+PF^-_6) = 5 \times 10^{-4}M$

Benzoyl peroxide (M)	Conversion (%)	$R_p \times 10^4$ (M. sec.$^{-1}$)	$C^+ . 10^4$ (M)
4×10^{-3}	10.35	3.9	3.01
6×10^{-3}	13.0	4.92	3.79
8×10^{-3}	15.77	5.95	4.59
10^{-2}	16.41	6.2	4.78
1.2×10^{-2}	18.7	7.45	5.74
1.4×10^{-2}	19.17	7.25	5.58

*Polymerizations were carried out as indicated previously but in these cases propagation time was 70 minutes.

TABLE IV.
POLYMERIZATION[a] OF THF (BULK)
(Benzoyl peroxide) $= 5 \times 10^{-3}$M

$Ph_2 I^+PF_6^-$ (M)	Conversion (%)	$R_p \times 10^4$ (M.sec.$^{-1}$)	$C^+ \times 10^4$ (M)
2×10^{-3}	0	—	—
4×10^{-3}	3,88	1.46	1.13
6×10^{-3}	8.23	3-11	2 39
10^{-2}	9.89	3.74	2.88
$1,2 \times 10^{-2}$	11.81	4 46	3.44
$1,6 \times 10^{-2}$	24.5	9 26	7.14

[a]Polymerizations were carried out as described in Table III.

As it can be seen from Figure I activation efficiency of benzoyl peroxide is higher then $PhN=NCPh_3$ at constant concentration of the salt. This means that the consumption of the salt is higher in latter case since two different types of radical are formed. On the other hand, when additional salt is supplied the efficiency of the azo compound increases (Figure 2). Initial radicals and propagating cations in all cases are represented in Table V.
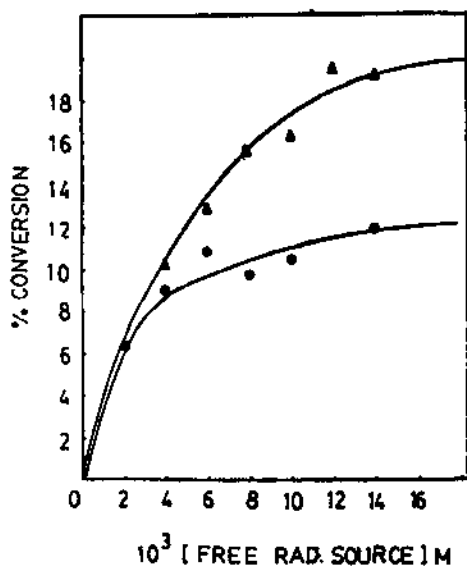

10^3 [FREE RAD. SOURCE] M

FIGURE 1. Effect of [Free rod. source] on the cationic polymerization of THF at fixed [Ph₂ I⁺PF₆⁻] $= 5 \times 10^{-3}$ M; ▲ Benzoyl Peroxide, ● PhN=NCPh₃.

10^3 [Ph₂I⁺PF₆⁻]M
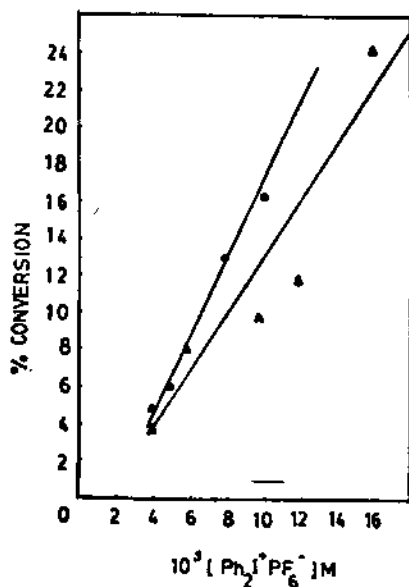
FIGURE 2. Effect of [Ph₂ I⁺PF₆⁻] on the cationic polymerization of THF at fixed [Free rad. source] $= 5 \times 10^{-3}$ M; ▲ Benzoyl peroxide, ● PhN = NCPh₃

TABLE V.

Free radical source	Radicals formed	Propagating cations
PhN=NCPh₃	Ph• + Ph₃C•	$+ Ph_3C^+$
Benzoyl Peroxide	PH•	
AIBN	$(CH_3)_2 - \underset{CN}{\overset{}{C}}•$	

The results obtained from moleculer weight determinations are entirely consistent with the above assumptions. (Table VI.) Polymers with high moleculer weight were obtained when benzoyl peroxide and AIBN utilized since active centres produced only by hydrogen abstraction may grow to much longer chain lenghts than those produced from Ph₃C. and Ph. radicals.

TABLE VI.

MOLECULAR WEIGHT RANGE OF POLYMERS

Free Radical Source	$\overline{M}_n \times 10^{-3}$
PhN=NCPh₃	15.0 — 79.3
Benzoyl Peroxide	200.7 — 1309.1
AIBN	500.6 — 1385.5

The most common free radical source, AIBN, produced high molecular weight polymers with comparatively low conversions (4—7 %).

CONCLUSIONS

The method outlined is excellent for cationic polymerization utilizing thermally stable salts in the presence of free radical initiators. These results allow selection of free radical initiators to produce polymers in the thousands to million molecular weight with desired rate. Detailed studies are now in progress to develop these ideas further using both thermal and photochemical sources of free radicals.

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