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Photochemical and thermal cationic polymerizations promoted by free radical initiators

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In the accompanying communication[1] we have indicated the supporting evidence for a proposed oxidation of electron donor free radicals to corresponding carbocations. The overall process envisaged may be represented as:

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

and, if applicable to initiating and early propagating intermediates in free radical polymerization, would result in the formation of initiating or propagating species for cationic polymerizations. Such processes would have considerable value in the design of photocurable cationic systems required for surface coatings, printing plate manufacture, etc., and we now report preliminary results which provide experimental support.

Recently there has been a significant growth of interest in the use of aryl diazonium salts[2] ($ArN_2^+X^-$), diaryl iodonium salts[3] ($Ar_2I^+X^-$) and triaryl sulphonium salts[4] ($Ar_3S^+X^-$) as photochemical initiators for cationic polymerizations of epoxides, alkyl vinyl ethers and other related monomers. With the exception of aryl diazonium salts, which are known to decompose thermally at moderately elevated temperatures[5], the other types of cationic salt ($X^- = PF_6^-, SbF_6^-, AsF_6^-$, etc.) are essentially thermally stable and unreactive to many cationically polymerizable monomers. In contrast all three types of salt yield cationic species on u.v. irradiation and the simple aryl homologues have absorption maxima below 300 nm with little or no photoactivity at wavelengths above the glass cut-off point. We have noted[1] that electron transfer to these cations results in fragmentation with the formation of aryl radicals and, if the reducing species is a suitable initiating or propagating free radical, a *chain reaction* for formation of cations will ensue provided that cationically polymerizable monomers are present, e.g. for polymerization of alkyl vinyl ethers (equations 2).

In principle, it should not matter whether the initiating free radical (X·) is obtained by thermal or photochemical (or any other) means. Both types of radical source have been studied in order to support the mechanistic ideas (thermal initiation) and to outline the scope for practical u.v. curing systems.

It is probable that atmospheric oxygen will interfere with radical promoted cationic polymerization by the usual peroxide forming processes – preliminary results suggest that the effect is greatest for alkyl vinyl ethers – and each system will need to be considered individually.

THERMAL PROMOTION OF CATIONIC POLYMERIZATION BY FREE RADICAL INITIATORS

Monomers chosen for study were tetrahydrofuran and n-butyl vinyl ether. Polymerizations were performed in vacuum, outgassed systems and purification procedures were those conventionally used for cationic polymerizations[6]. Representative results are given in *Tables 1* and *2* and it must be stressed that the data are not optimized in any way and conversions to polytetrahydrofuran were deliberately kept very low so as to permit easy handling of the very viscous solutions obtained.

For n-butyl vinyl ether electron donor, free radicals are obtained by

$$X\cdot + CH_2{=}CHOR \longrightarrow XCH_2\dot{C}HOR \text{ etc.}$$

$$\sim\!\sim CH_2\dot{C}HOR + Ar_2I^+PF_6^- \longrightarrow \sim\!\sim CH_2CH{=}\overset{+}{O}R\ PF_6^- + ArI + Ar\cdot \qquad (2)$$

$$Ar\cdot + CH_2{=}CHOR \longrightarrow ArCH_2\dot{C}HOR \text{ etc.}$$

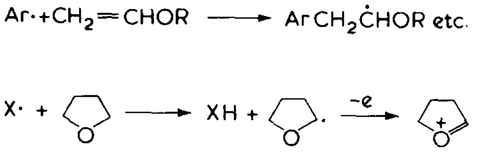
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Table 1 Thermal polymerization[a] of tetrahydrofuran (bulk)

Free radical source (M)	Cation salt (M)	Heating time (min)	Conversion (%)
AIBN, 10^{-2}	$(pCH_3C_6H_4)_2I^+PF_6^-$, 5×10^3	110	5.3
Benzoyl peroxide, 10^{-2}	5×10^3	60	3.7[b]
None	5×10^3	110	0
$PhN{=}NCPh_3$, 5×10^{-3}	5×10^3	110	10.0[c]
Benzpinacol, 10^{-3}	5×10^3	60	16.7[c]

[a] Polymerizations were carried out by heating the reaction mixtures at 70°C for the times indicated; polymer was obtained by precipitation into water containing a little base; [b] $\bar{M}_n$ = 119 730 this is a typical molecular weight for the polytetrahydrofuran samples obtained and consequently even the low conversions recorded represent extremely viscous, and sometimes solid, reaction mixtures; [c] Polymer was recovered by precipitation after standing overnight at room temperature

Table 2 Thermal polymerization of n-butyl vinyl ether in bulk[a] at 50°C

Free radical source (M)	Cation salt (M)	Reaction time (h)	Conversion (%)
None	$(pCH_3C_6H_4)_2I^+PF_6^-$, 5×10^{-3}	3.0	0
AIBN, 5×10^{-3}	None	3.0	0
AIBN, 5×10^{-3}	$(pCH_3C_6H_4)_2I^+PF_6^-$, 5×10^{-3}	3.0	75[b]

[a] In order to maintain solutions of the cation salt reaction mixtures contained 10 vol % CH_2Cl_2; [b] the tacky polymer was obtained by precipitation into methanol containing a small amount of base

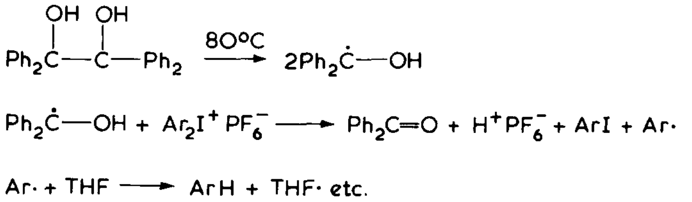
Table 3 Photochemical polymerization[a] of tetrahydrofuran (bulk) at 25°C (pyrex glass vessels)

2,2-Dimethoxy-2-phenyl acetophenone (M)	p-$ClC_6H_4N_2^+PF_6^-$ (M)	Irradiation time (min)	Conversion (%)	$10^{-3}\bar{M}_n$
5×10^{-3}	5×10^{-3}	30	7.5	38.9
5×10^{-3}	5×10^{-3}	45	10.5	46.1
5×10^{-3}	5×10^{-3}	60	17.9	79.9
0	5×10^{-3}	45	1	51.8
10^{-3}	5×10^{-3}	45	4.3	50.9
5×10^{-3}	5×10^{-3}	45	10.5	46.1
10^{-2}	5×10^{-3}	45	15.0	24.2
5×10^{-3}	10^{-3}	45	3.7	33.4
5×10^{-3}	5×10^{-3}	45	10.5	46.1
5×10^{-3}	10^{-2}	45	11.9	52.7

[a] Polymer samples were recovered as indicated in *Table 1* but in these cases the irradiation time was the total reaction time. Molecular weights were determined by membrane osmometry in toluene solutions

radical addition to the monomer, as indicated above, whilst for polymerization of THF and other cyclic ethers the important reducing species must be obtained by hydrogen abstraction (equation 3).

The data of *Tables 1* and *2* clearly provide experimental substantiation of the ideas presented in the previous communication[1] and illustrate the range of common free radical sources which may be used to promote cationic polymerizations. Of particular interest is the use of benzpinacol as a thermal source of $Ph_2\dot{C}{-}OH$ radicals. By analogy with other electron transfer reactions of these intermediates[7], it is highly probable that protonic acid is produced, offering a new, relatively high temperature source of cationic initiators (equations 4).



$$Ph_2C(OH){-}C(OH)Ph_2 \xrightarrow{80^{\circ}C} 2Ph_2\dot{C}{-}OH$$

$$Ph_2\dot{C}{-}OH + Ar_2I^+PF_6^- \longrightarrow Ph_2C{=}O + H^+PF_6^- + ArI + Ar\cdot \qquad (4)$$

$$Ar\cdot + THF \longrightarrow ArH + THF\cdot \text{ etc.}$$

Phenylazotriphenyl methane is another special case since the expected product of thermolysis ($Ph_3C\cdot$) has been shown[1] to undergo oxidation to Ph_3C^+ and the latter is a well-known initiator for cationic polymerization[6].

PHOTOCHEMICAL PROMOTION OF CATIONIC POLYMERIZATION BY FREE RADICAL INITIATORS

In recent years there has been a dramatic increase in the utilization of photoactive initiators for u.v. curing of surface coatings and many related applications[8,9]. Of the photoinitiator systems widely employed, benzoin and its alkyl ethers and alkoxyacetophenones are especially useful since they absorb light up to approximately 380 nm and fragment with high quantum efficiencies[9]. Azo compounds are also photochemically active initiators but with rather low extinction coefficients in the regions above the glass cut-off point. As we have already noted, aromatic carbonyl compounds generally, and aliphatic azo compounds, are readily selectively excited in the presence of simple aryl-diazonium, -iodonium, and -sulphonium salts by the simple expedient of using glass vessels. Appropriate wavelength filters may also be used. Photochemically-induced polymerizations were carried out as for the thermal reactions except that the reaction vessels (1 cm diameter glass tubes) were irradiated by means of a 250 watt medium pressure mercury lamp whilst maintained in a water bath at 25°C.

Table 3 gives data for a series of polymerizations of THF utilizing p-chlorphenyldiazonium PF_6^- as cationic salt and 2,2-dimethoxy-2-phenyl acetophenone (a commercial u.v. curing agent) as source of free radicals. These preliminary data are interesting in illustrating a possible rate saturation effect for the diazonium salt [identical behaviour was observed using $(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$] and the expected rate and molecular weight dependencies on both the time of polymerization and the concentration of free radical initiator. A particular advantage in the use of alkoxyacetophenones and benzoin alkyl ethers is that of the two primary photofragments, one is a powerful electron donor radical which should oxidize to the corresponding cation even more easily than similar radicals derived from the monomers (equations 5). This assures formation of an initiating cation without the requirement for hydrogen abstraction or addition to monomer.

Table 4 gives representative data for promoted photopolymerization of THF with a wide range of photoactive radical sources and it is interesting to

Table 4 Photochemical polymerization[a] of tetrahydrofuran (bulk) at 25°C (pyrex glass vessels)

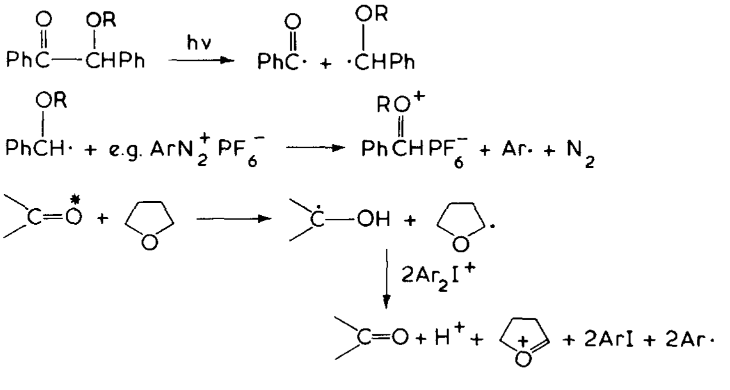
Photoactivator (M)	Cation salt (M)	Irradiation time (min)	Conversion (%)	$10^{-3}\bar{M}_n$
2,2-Dimethoxy-2-phenyl acetophenone 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	45	10.5	46.1
None	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	45	~1	51.8
2,2-Dimethoxy-2-phenyl acetophenone 5×10^{-3}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	50	13.4	
None	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	50	<1	
2,2-Dimethoxy-2-phenyl acetophenone 5×10^{-3}	$(C_6H_5)_3S^+PF_6^-$ 10^{-3}	150	5.7[b]	54.6
None	$(C_6H_5)_3S^+PF_6^-$ 10^{-3}	150	~1[b]	
Benzoin ethyl ether 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	60	4.4	
2,2-diethoxyacetophenone 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	60	4.4	
Benzoin 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	45	4.7	
N-Bromosuccinimide 5×10^{-3} M	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	120	4.6	24.3
$PhN{=}NCPh_3$ 5×10^{-3}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	56	3.1[c]	177.5
Benzophenone 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	45	3.1	
Benzil 5×10^{-3}	p-$ClC_6H_4N_2^+PF_6^-$ 5×10^{-3}	45	2.4	
2-tert-Butyl anthraquinone 5×10^{-3}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	60	2.0	
2-Chlorothioxanthone 5×10^{-3}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	60	4.2	
Maleic anhydride 10^{-1}	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ 5×10^{-3}	180	7.5	

[a] Polymers were obtained and molecular weights determined as described in *Table 3;* [b] reaction mixture contained 20 vol % CH_2Cl_2;
[c] Reaction mixture left overnight at r.t. before precipitation of polymer

Table 5 Photochemical polymerization of n-butyl vinyl ether bulk at 25°C (λ = 366 nm)

2,2-Dimethoxy-2-phenylacetophenone (M)	$(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ (M)	Irradiation time (min)	Conversion (%)
5×10^{-2}	None	10	0
None	5×10^{-3}	10	0.8
5×10^{-2}	5×10^{-3}	10	98[a]

[a] Polymer was precipitated at the end of photolysis as described in *Table 2*



(5)

(6)

note the activity of benzophenone, benzil, 2-tert-butyl anthraquinone, and 2-chlorothioxanthone. These molecules are well known[10,11] to undergo photo-induced hydrogen abstraction reactions with THF and cation formation would then follow as described previously (for example, equation 6).

Similarly the known[12] free radical abstraction process occurring when maleic anhydride is irradiated in THF is readily diverted to formation of propagating cations by diaryl iodonium salts.

Table 5 gives perhaps the most convincing data for free radically-promoted cationic polymerization and points the way to other related promotor systems for photochemically-induced processes.

GEL FORMATION IN A BIS-EPOXIDE

As a very simple but crude demonstration of the possible value of free radical promotion of cationic polymerization, several experiments were performed using 1,2-epoxyethyl-3,4-epoxycyclohexane as the polymerizable monomer. Because of the presence of two epoxide groups, this monomer readily crosslinks and ultimately forms gelled systems. In a typical experiment, photolysis through glass of bulk monomer containing 5×10^{-3} M $(p\text{-}CH_3C_6H_4)_2I^+PF_6^-$ formed a gel after 84 min. The same system containing 5×10^{-3} M $PhCOC(OMe)_2Ph$ formed a gel after about 10 min – clear evidence for the promoting effect of the free radical source.

CONCLUSIONS

Preliminary experimental results fully support the idea that suitable free radical sources in combination with oxidizing cations may be used to promote cationic polymerization of alkyl vinyl ethers and cyclic ethers. Mechanistic details remain to be evaluated but for all systems studied, an important feature is the generation of a chain reaction leading to formation of cationic initiators with obvious implications to quantum amplification in photo-induced phenomena. Detailed studies of individual systems are now in progress and it is clear that other types of cationically susceptible monomers may react similarly given appropriate matching of redox potentials for the promoting free radicals and the oxidizing salts.

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Thermal and mechanical properties of isotactic random propylene–butene-1 copolymers

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INTRODUCTION

The morphology, the crystal structure and the thermal behaviour of solution grown crystals of isotactic propylene–butene-1 copolymers (PP–PB) have been investigated by Martuscelli and coworkers and compared with those of homopolymers[1]. The dissolution temperature, the density and the apparent enthalpy of fusion showed eutectic behaviour with a minimum at a composition of about 48% by wt in butene-1. The crystallinity, present at all compositions, was attributed to the principal homopolymer crystalline phase. In the middle composition range both polybutene-1 (form I) and polypropylene crystalline phase occurred[1]. The experimental results indicated that isotactic PP–PB crystallizable copolymers show a crystal phase inversion for a composition of about 50%. A similar phase inversion has been found by Turner-Jones in the case of melt crystallized materials[2].

The present Note describes investigations on the thermal and tensile behaviour of compression-moulded samples of isotactic PP–PB copolymers.

EXPERIMENTAL

The unfractionated isotactic random copolymer samples used in the present investigation (see *Table 1*) were obtained by copolymerization reactions carried out with a $TiCl_3–AlEt_2Cl$ catalyst.

The composition of the samples range from pure isotactic polypropylene to pure isotactic poly(butene-1). All copolymers are crystallizable in the range of compositions examined.

The composition of the copolymers was determined by i.r. analysis.

A Perkin–Elmer differential scanning calorimeter DSC-2 was used to obtain apparent heats of fusion ΔH_f^*. All samples were heated at 20°C/min. The area under the melting d.s.c. trace was integrated and expressed in cal/g using a calibration factor determined from melting a known weight of indium for which a value of 6.8 cal/g was taken as the heat of fusion.

The melting temperatures of the samples were measured from the maxima in the d.s.c. endotherms. The temperature scale was calibrated from the melting points of low molecular weight standard samples.

The copolymers were tested mechanically using an Instron Universal Testing Equipment Model II22. Dumb-bell shaped specimens were prepared by compression moulding and quickly cooled to room temperature: the specimens of polypropylene were obtained by compression moulding at $P = 300$ kg/cm^2 and $T = 200°$C; the speimens of poly(butene-1) at $P = 300$ kg/cm^2 and $T = 160°$C and the specimens of copolymers at $P = 300$ kg/cm^2 and $T = 160°$C. The experiments were carried out at a strain rate of $\dot{\epsilon} = 0.9$ min^{-1} at room temperature.

RESULTS AND DISCUSSION

Thermograms of melt-crystallized samples of isotactic PP–PB copolymers and of pure homopolymers show a

Table 1 Composition of isotactic random propylene–butene-1 copolymers

Sample	Butene-1 content	
	wt %	mol %
PP	0	0
PP–PB–5	45.6	38.6
PP–PB–6	47.9	40.8
PP–PB–7	53.3	46.1
PP–PB–8	70.0	63.6
PB	100	100

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