Polymer Bulletin 19, 461–467 (1988)

Polymer Bulletin

Photo-initiated cationic polymerisation for use in paper preservation

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Summary

Polymer films were deposited on paper by a photoinitiated cationic process. These films possessed enhanced resistance to deterioration by folding and acid-aging.

Introduction

A variety of actors contribute to the degradation of papers and documents. Light, temperature, humidity and type of sizing agent are important in addition to mechanical sources of deterioration involved in lending and photocopying.[1] The prime offender however is decay by acid (sulphuric and nitric) from atmospheric pollution. Acid hydrolysis of cellulose reduces its chain length by one tenth at ph5.6

Methods of preservation adopted to date have been uneconomical[2] or, restricted by the nature of the reactants.[3] Photoinitiated cationic polymerisation represents a departure from these restrictions. A wide range of initiator/monomer systems are available which function at room temperature in the presence of oxygen and use conventional sources of ultraviolet radiation.[4]

In this study we have used the photoinitiator 4,4' -dimethyldiphenyliodonium hexaflurophosphate (4,4' -DMDPI) in conjunction with a variety of monomers to prepare films on paper which display good resistance to acid and superior mechanical properties.

Experimental

Materials

The initiator, 4,4' -DMDPI, was prepared by the reaction of an aqueous solution of the iodide[5] with aqueous ammonium hexaflurophosphate. The recrystallised product (from 25/75 vol. methanol/water) was a white solid (33% yield, m.p. 170°-2°C) possessing a λ_{max} in methanol at 239nm (ϵ=7, 453).

Monomers 2-chloroethyl vinyl ether (2-CEVE), ethyl vinyl ether (EVE), n-butyl vinyl ether (BVE), epichlorohydrin (ECH), cyclohexene oxide (CO), styrene oxide (SO) and diallylamine (DAA) were all obtained from Aldrich and were dried over calcium hydride prior to distillation under nitrogen atmosphere. Propylene oxide (PO) was distilled in vacuo before use. Styrene (S) and ethyl acrylate (EA) monomers were treated with aqueous sodium hydroxide, washed with water, dried over calcium chloride then calcium hydride prior to distillation. Methyl methacrylate (MM) was treated with aqueous sodium carbonate, washed with water, dried over magnesium sulphate then calcium hydride prior to distillation. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dicyclopentadiene (DCPD) from

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Aldrich was distilled under reduced pressure, ε-caprolactam (ε-CM) was recrystallised twice from cyclohexane and dried in vacuo. 1,3-butadiene (1,3-BD) from Cambrian Chemicals was distilled in vacuo from successive sodium mirrors. Allylcyclohexane (ACH) was prepared by a conventional Grinard synthesis.[6] Diallyldiphenylsilane (DADPS) and diallylmethylsilane (DAMS) were donated by E.B. Kronfli.[7]

UV

UV radiation was supplied by a Rayonet Preparative Reactor-208. Four RUL-300nm and four RUL-350nm lamps provided maximum emissions at 300nm and 350nm respectively with a total output of 100W.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was carried out using a JEOL JSM-35C. Samples were mounted on aluminium studs and coated with gold to ensure good electrical conductivity.

Fold Endurance & Acid-Aging

Fold endurance measurements were carried out on a M.I.T. fold endurance tester. Samples (15mm wide) are bent through 270° under 0.5kg tension until failure; 50% relative humidity and a temperature of 23°C ±1°C are maintained throughout.

Two types of acid-aging procedures were adopted. The samples were either treated with 40% vol/vol sulphuric acid until complete disintegration occurred, or treated with acids of varying strengths (10%, 30% vol/vol sulphuric acid) for different lengths of time prior to examination by fold endurance.

Liquid-Phase Polymerisation

Monomers were pipetted under nitrogen into pyrex ampoules containing the initiator 4,4'-DMDPI to give 1% wt./vol solutions. After degassing and sealing, the ampoules were opened, the polymerisation terminated by the addition of cold methanol/ammonium hydroxide and the polymers precipitated in methanol and filtered. Polymers were reprecipitated from methanol.

In-Situ Liquid-Phase Polymerisation

Sheets of Whatmanns No.1 filter paper (1.5 x 12cm) were washed with acetone prior to use. The single sheets were immersed in a 4,4'-DMDPI/monomer solution (1% wt./vol), placed in individual stoppered test tubes and exposed to UV radiation at 20°C. After irradiation the papers were dipped in methanol and dried in vacuo at room temperature.

In-Situ Vapour-Phase Polymerisation

Whatmanns sheets (batches of six) were immersed in a 4,4'-DMDPI/acetone solution (1% wt./vol) prior to air-drying for thirty minutes. The required volume of degassed monomer was transferred in vacuo to a pyrex pressure vessel (fig.1) at liquid nitrogen temperature, containing the paper sheets. The vessel was brought to room temperature and left to equilibriate for twenty-four hours prior to exposure to UV radiation at 20°C.

Results

Liquid-Phase Polymerisation

4,4'-DMDPI initiated the polymerisation of some of the monomers, but not others. Table 1 indicates which monomers were polymerised by this initiator, the time at which conversion reached its maximum and the percentage conversion. Curves depicting percentage conversion to polymer against irradiation time are given in figs.2-5. The reactivity of monomer to 4,4'-DMDPI followed the order 2-CEVE, EVE, BVE>S>EA>SO>ECH>PO>THF>S-MM>DADPS.

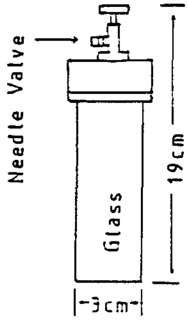

Fig.1: Vapour-phase polymerisation apparatus.

The isolated polymers varied in appearance and consistency. Poly(PO) and poly(ECH) were transparent rubbers; poly(EA) was a white rubber. Poly(S), poly(S-MM) and poly(DADPS) were white solids. Poly(2-CEVE), poly(EVE) and poly(BVE) were pale brown tacky rubbers. Poly(CO) was a pale brown flaky material and poly(SO) a bright yellow crystalline solid. Poly(THF) was a tan-coloured leathery material.

Monomer	Polymer formed	% Conversion to polymer	Irrad. time	Monomer	Polymer formed	% Conversion to polymer	Irrad. time
2-CEVE	+	100	120sec.	THF	+	62	7hr.
EVE	+	"	"	S-MM	+	3	1hr.
BVE	+	95	"	DADPS	+	2	3hr.
SO	+	88	1hr.	DAMS	-	-	-
ECH	+	82	"	DAA	-	-	-
CO	+	92	30mins.	ACH	-	-	-
PO	+	100	2hr.	DCPD	-	-	-
S	+	"	1hr.	1,3-BD	-	-	-
EA	+	95	"	ε-CM	-	-	-

Table 1: Polymerisation of monomers by 4,4'-DMDPI initiator

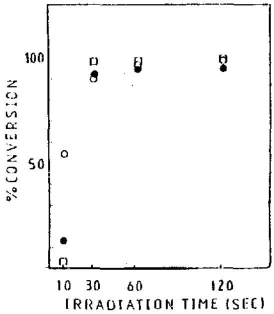

Fig.2: Conversion to polymer against irradiation time for 2-CEVE (□), EVE (○) and BVE (●)

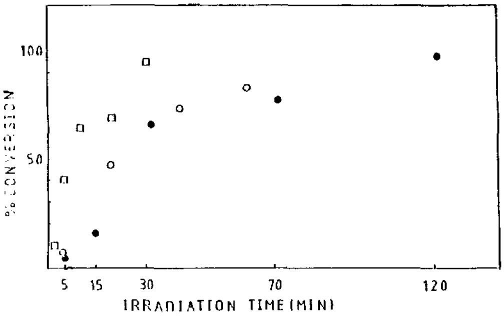

Fig.3: Conversion to polymer against irradiation time for CO(□), ECH(○), and PO(●).

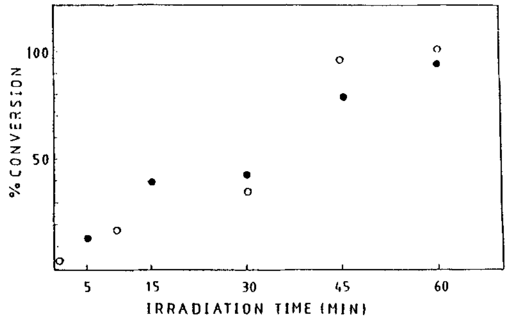

Fig.4: Conversion to polymer against irradiation time for S(○) and EA(●).

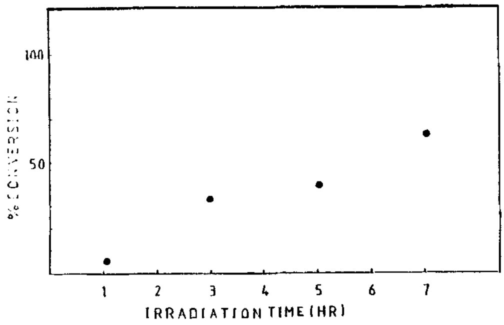

Fig.5: Conversion to polymer against irradiation time for THF.

In-Situ Liquid-Phase Polymerisation

Of the monomers polymerisable by 4,4'-DMDPI, only CO, SO and ECH were capable of forming polymer films on the paper surface. Percentage weight increases per sheet were poly(CO) = 85%, poly(SO) = 76% and poly(ECH) = 87%. Visible evidence of film formation was seen under SEM. SEM photographs of the coated papers, under high magnification (x1800), are shown in figs. 6-8. For comparison, untreated paper is shown in fig.9. Polymer is evident even at low magnifications (x200).[8]

The appearance of each film under SEM is different. Poly(CO) presents a smooth film at high magnification with polymer filling the spaces between fibres (fig.6). Poly(ECH) coated at equivalent weight increases per sheet to poly(CO) reveals the polymer adhering to and connecting the individual fibres (fig.7). Paper coated with poly(SO) aptly demonstrates how the polymer connects individual fibres of the paper substrate (fig.8).

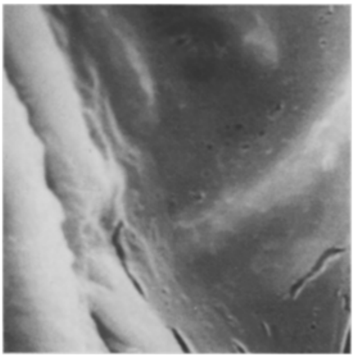

Fig.6: SEM photo of poly(CO) -coated paper (mag.x1800).

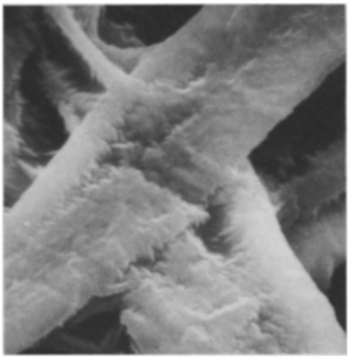

Fig.7: SEM photo of poly(ECH) -coated paper (mag.x1800).

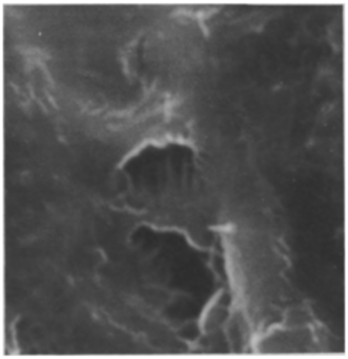

Fig.8: SEM photo of poly(SO) -coated paper (mag.x1800).

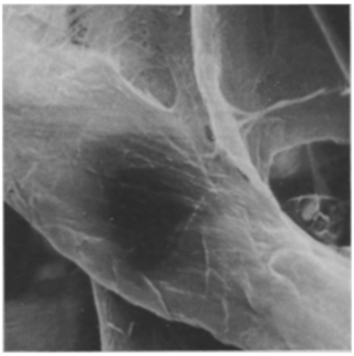

Fig.9: SEM photo of untreated paper (mag.x1800).

In-Situ Vapour-Phase Polymerisation

Only monomers EVE and PO were capable of forming polymer films from monomer in the vapour phase. Percentage weight increases per sheet were; poly(EVE) = 60%, poly(PO) = 55%. No attempt was made to polymerise these monomers by the in-situ liquid-phase process since the vapour-phase process was the preferable of the two. EVE was chosen as the most suitable vinyl ether in view of its low boiling point (33°C). High magnification SEM photos of paper coated by these two polymers are shown in fig.10 & 11. As seen, their appearance is different even at similar weight increases.

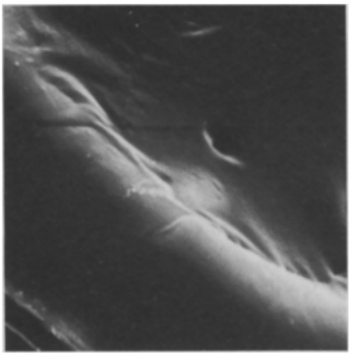

Fig.10: SEM photos of poly(EVE) -coated papers (mag.x1800).

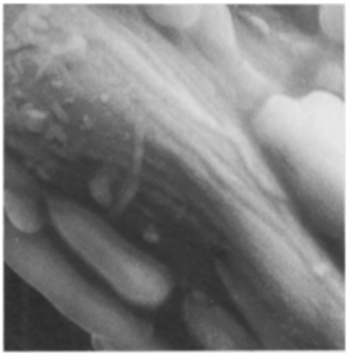

Fig.11: SEM photos of poly(PO) -coated papers (mag.x1800).

Degradation Experiments

All coated papers, poly(CO), poly(SO), poly(ECH), poly(PO) and poly(EVE) were submitted to fold endurance testing and treatment with 40% vol/vol sulphuric acid at 65°C. The results are shown in table 2. It was evident that films prepared using epoxy monomers which possess an intact ring structure after polymerisation offer the most resistance to fold and acid aging i.e. poly(CO) and poly(SO). The other polymers appear to reduce the crystalline regions of the paper, facilitating acid degradation.

Treatment of poly(EVE) -coated paper with 30% vol/vol and 10% vol/vol sulphuric acid for different lengths of time prior to fold endurance testing, result in the trends shown in fig.12. Though substantially weaker than untreated paper, the pattern of acid degradation is clear. The initial steepness of the trend is due to the amorphous regions of the paper being attacked first, while the crystalline regions prove more arduous to the acid.

Polymer Film	Fold Value[a] (±10)	Acid Resistance[b] (min.)
poly(CO)	330	30
poly(SO)	240	20
poly(ECH)	17	-5
poly(EVE)	10	-5
poly(PO)	10	-7
untreated	43	0

a: of non acid-degraded samples
b: 40% vol/vol sulphuric acid at 65°C

Table 2: Resistancy of coated papers to fold endurance testing and acid-aging.

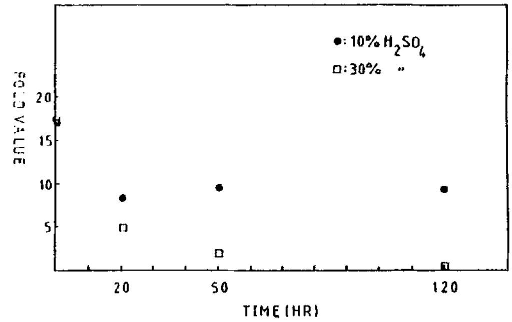

Fig.12: Fold endurance value against acid degradation time for poly(EVE) -coated paper.

Conclusions

The photoinitiator 4,4' -dimethyldiphenyliodonium hexaflurophosphate has been used to polymerise a variety of monomers. Several of these systems may be used to deposit acid-resistant films on paper by a liquid or vapour-phase process. Systems involving poly(cyclohexene oxide) and poly(styrene oxide) are potentially the most useful, giving treated papers an increased resistance to fold and acid-aging.

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Acknowledgements

We wish to thank Dr. M. Burstall, Dr. C.C. Mollett and Mrs. C.E. Butler of the University of Surrey Ink Unit for the fold endurance measurements and assistance. Financial support was provided by the British Library.

Accepted February 1, 1988 C