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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 factors 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 acids (sulfuric 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 which function at room temperature in the presence of oxygen and use conventional sources of ultraviolet radiation is available.[4]

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

Experimental

Material

The initiator, 4,4'-DMDPI, was prepared by the reaction of an aqueous solution of the iodide[5] with aqueous ammonium hexafluorophosphate. 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 239 nm of ϵ = 7,453.

2-Chloroethyl vinyl ether (2-CEVE), ether 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 a nitrogen atmosphere. Propylene oxide (PO) was distilled in vacuo before use. Styrene (S) and ethyl acrylate (EA) were treated with aqueous sodium hydroxide, washed with water, dried over calcium chloride and then calcium hydride prior to distillation. Methyl methacrylate (MM) was treated with

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** Present address: EniChem Elastomers Ltd., Hardley, Hythe, Southampton, UK aqueous sodium carbonate, washed with water, dried over magnesium sulphate and then calcium hydride prior to distillation. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dicyclopentadiene (DCPD) from 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 Grignard 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, respecively, 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 & Agid-Aging

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

Two types of acid-aging procedures were adopted. The samples were treated either with 40% vol/vol sulphuric acid until complete disintegration occurred, or with acids of varying strengths (10%, 30% vol/vol sulfuric 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, polymerisation was performed, after which the ampoules were opened and the polymerisation terminated by the addition of cold methanol/ammonium hydroxide. The polymers were precipitated in methanol and filtered. Polymers were reprecipitated from methanol.

In-Situ Liquid-Phase Polymerisation

Sheets of Whatman's 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

Whatman's 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 and left to equilibriate for twenty-four hours prior to exposure to UV radiation at 20°C.

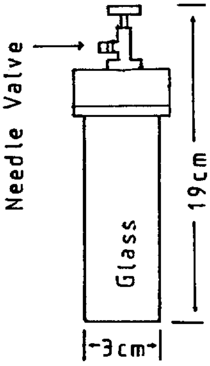

Fig.1: Vapour-phase polymerisation apparatus.

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 polymers are given in figs.2-5. The reactivity of monomers to 4,4-DMDPI followed the order 2-CEVE, EVE, BVE>S>EA> SO>ECH>PO>THF>S-MM>DADPS.

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.

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

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	+	100	1hr.	1,3-BD	-	-	-
EA	+	95	"	ε-CM	-	-	-

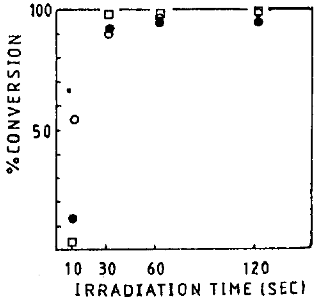

Fig.2: Conversion to polymer against irradiation time for 2-CEVE (□), EVE (○) and BVE (●).

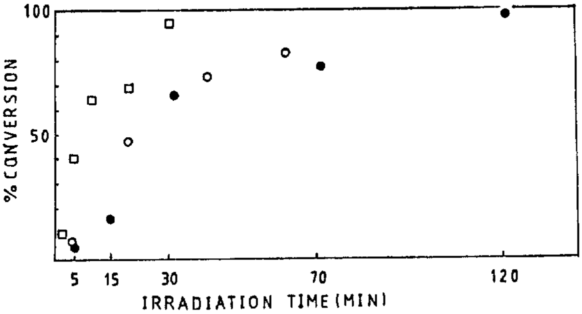

Fig.3: Conversion to polymer against irradiation time for CO (□), ECH (○), and PO (●).

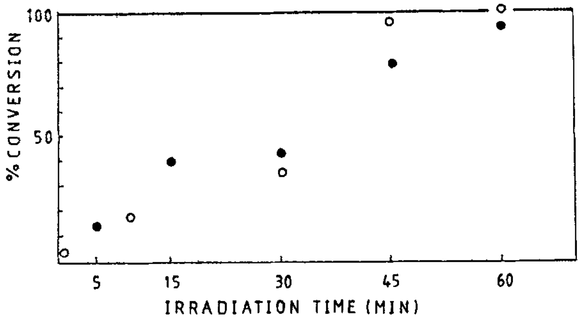

Fig.4: Conversion to polymer against irradiation time for S (○) and EA (●).

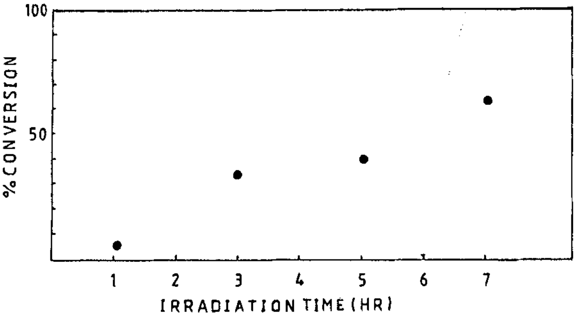

Fig.5: Conversion to polymer against irradiation time for THF.

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) = 86%, 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 distinctive. 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 the individual fibres of the paper substrate (fig.8).

In-Situ Vapour-Phase Polymerisation

Only the 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 appearances are different, even at similar weight increases.

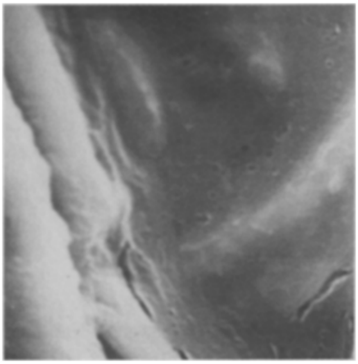

Fig.6: SEM photo of poly(CO)-coated paper (mag.x1800).

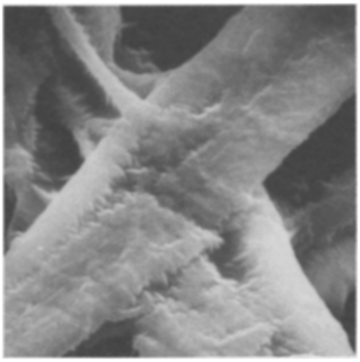

Fig.7: SEM photo of poly(ECH) -coated paper (mag.x1800).

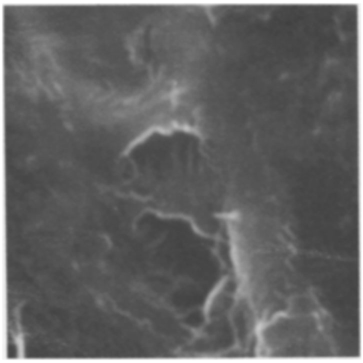

Fig.8: SEM photo of poly(SO)-coated paper (mag.x1800).

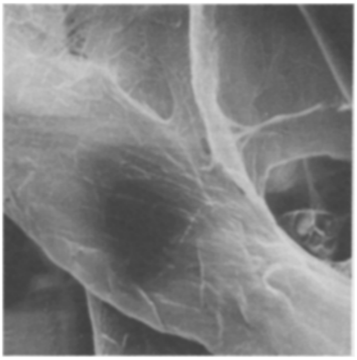

Fig.9: SEM photo of untreated paper (mag.x1800).

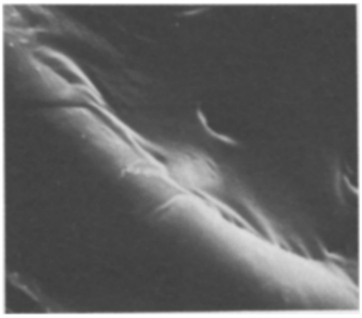

Fig.10: SEM photos of poly(EVE) -coated papers (mag.x1800).

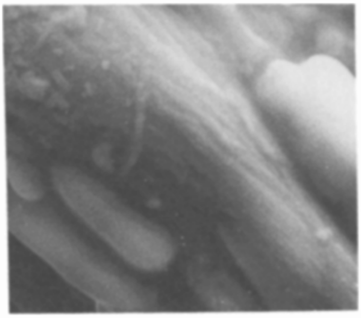

Fig.11: SEM photos of poly(PO) -coated papers (mag.x1800).

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 sulfuric 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, i.e. poly(CO) and poly(SO), offer the most resistance to fold and acid aging. The other polymers appear to reduce the level of crystallinity of the paper, facilitating acid degradation.

Treatment of poly(EVE)-coated paper with 30% vol/vol and 10% vol/vol sulfuric acid for different lengths of time prior to fold-endurance testing, results in the trends shown in fig.12. Though substantially weaker than with 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 resistent to the acid.

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

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 sulfuric acid at 65°C

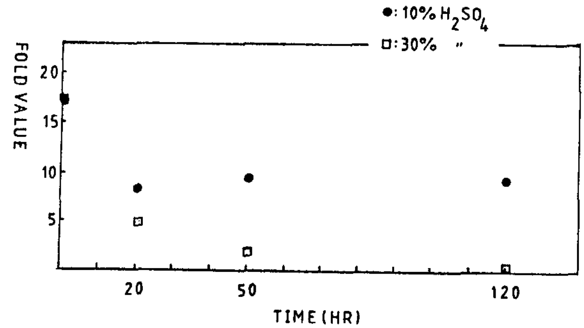

Fig.12: Fold-endurance value against acid degradation time for poly(EVE)-coated paper.

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 folding and acid-aging.

References

1. Seeley, N., Barker, N., Chemistry in Britain, 15, No.6, 305 (1979)
2. Barrow, W.J., Permanance/durability of the book-VII; physical and chemical properties of book papers 1507-1949. Richmond Va.; Research Laboratory Inc., (1974)
3. Williams, J.C., Kelly, G.B., U.S. Patent No. 3939091, 5 August, (1975)
4. Crivello, J.V., in "UV Curing Science & Technology", ed. by S.P. Pappas, Technology Marketing Co., Stamford, Connecticut, Chap.2, (1978)
5. Beringer, F.M., Drexler, M., Gindler, E.M., Lumpkin, C.C., J. Am. Chem. Soc., 75, 2705 (1953)
6. Ketley, A.D., Ehrig. R.J., J. Polym. Sci. A, 2, 4461 (1964).
7. Kronfli, E.B., D.Phil. thesis, University of Sussex, Falmer, UK (1971)
8. Wilson, D.J., D.Phil. thesis, University of Sussex, Falmer, UK (1983)

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