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Studies of moisture induced crosslinking in a novel vinyl ether-maleic anhydride copolymer

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SUMMARY

A novel vinyl ether, 2,2-dimethyl-4-vinyloxymethyl-1,3-dioxolane (DMVMD), that has a dimethyl ketal protected vicinal diol functionality, was synthesizied from readily available starting materials, such as glycerol, acetone and acetylene. Copolymerisation of DMVMD with maleic anhydride (MAH) in various molar ratios was carried out using a free radical initiator. The composition of the copolymer was established by conductometric titration, and was found to be 1:1 irrespective of the monomer feed composition thus establishing its alternating nature. The copolymer formed clear free standing films upon solvent casting which became insoluble upon prolonged exposure to ambeint atmosphere. The insolubility is ascribed to moisture induced crosslinking. A plausible mechanism for the crosslinking involves the hydrolysis of some of the anhydride groups, followed by acid catalysed deketalization, and then by the reaction of the alcoholic groups, thus generated, with the residual anhydride to give ester crosslinks. This hypothesis was confirmed both by model reactions and insitu FT-IR studies.

INTRODUCTION

Vinyl ethers are electron rich olefins that can be polymerized by cationic initiators. The recent discovery of living cationic polymerization methodology, using a combination of an initiator and a catalyst, has generated considerable interest in this class of monomers.[1] A wide variety of vinyl ethers that contain pendant masked functional groups have been synthesized and polymerized via this cationic process.[2] The objective of such studies often being the generation of amphiphilic block copolymers, one of the blocks of which contain polar functional groups, such as alcohols, amines and carboxylic acids, usually in a masked form.[3]

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Vinyl ethers can also be copolymerised with electron deficient olefins such as maleic anhydride, α-chloro acrylonitrile, alkyl maleimides etc., to give essentially alternating copolymers.[4] A wide variety of vinyl ethers have been copolymerized with maleic anhydride, with the motivation in most cases being the understanding of the underlying mechanism for the formation of such alternating copolymers. In some cases, however, the reactive anhydride functionality in the alternating copolymer backbone has been used to tether specific functional units, such as mesogens.[5] In this paper we report the synthesis of a novel vinyl ether monomer, DMVMD,[6] that has a pendant vicinal diol functionality which is protected as a dimethyl ketal, and its copolymerisation behaviour with maleic anhydride. The presence of both an acid-sensitive protecting group and an activated carboxylic acid derivative, namely the anhydride, in the same polymer renders this system potentially crosslinkable. Free standing films of these copolymers were indeed seen to undergo moisture induced crosslinking, a mechanism for which has been proposed based on some model reactions and direct FT-IR studies. Maleic anhydride based copolymers have been studied as potentially useful moisture curable binders and coatings in the recent patent literature.[7] However, unlike in the present investigation, in these studies the copolymer is taken along with compounds containing blocked amino groups which liberate free amines in the presence of water, which in turn causes crosslinking.

EXPERIMENTAL

General Procedures: ^1H NMR spectra were obtained on a Bruker ACF-200 MHz spectrometer. FT-IR spectra were recorded on a Bio-Rad FTS-7 spectrometer. Conductometric titrations were carried out using a Century CC603 digital conductivity meter. Maleic anhydride was purified by sublimation at 53°C/3mm. Benzene was rendered thiophene free by using conc.H_2SO_4, and was then freshly distilled from sodium. High pressure vinylation of isopropylidene glycerol (A) was carried out in a Parr pressure vessel. The monomer DMVMD was freshly distilled from CaH_2 before use. AIBN was recrystallized from methanol. 2,2-Dimethyl 1,3 dioxolane was distilled from sodium before use. Acetic acid was refluxed and distilled from P_2O_5, and acetic anhydride was fractionally distilled before use.

2,2-Dimethyl-4-hydroxymethyl-1,3-dioxolane(A) Glycerol (1mole), acetone (4 moles), PTSA.H_2O (0.004 mole) and petroleum ether 40-60°C (300 ml) were added to a 3-necked round bottomed flask. Water formed in the reaction was azeotropically removed using a Dean-Stark apparatus. After 24 h, the reaction mixture was neutralized using sodium acetate, filtered, concentrated and distilled under reduced pressure to obtain the product in 87% yield. B.P 80-81° C/11 mm.

2,2-Dimethyl-4-vinyloxymethyl-1,3-dioxolane(DMVMD) Isopropylidene glycerol (A) (106.7 g,100 ml), tetrahydrofuran (100 ml,solvent) and finely powdered KOH(4 g) were added to the reaction vessel of a high pressure reactor. The mixture was pressurized with acetylene-N_2 mixture to 25 atm. and the temperature was maintained at 150°C for 48 h.

The solid was filtered, the residue concentrated and subject to distillation under vacuum to give the monomer in 70% yield. The monomer was further purified by distillation over CaH_2 prior to polymerisation.

^1H NMR ($CDCl_3$) δ 1.38,1.42 (s,s,3H,3H, gem-dimethyl), δ 3.19-3.84 (m,2H,CH_2=CH-O-CH_2), δ 4-4.09 (M, 2H ,ring CH_2O), δ 4.15 (d,1H,CH_2=CH), δ 4.27 (d,1H,CH_2=CH), δ 6.48 (d,d 1H,CH_2=CH) .

Copolymerizations Monomers DMVMD (M_1) and maleic anhydride (M_2) (in various feed ratios) were taken along with benzene and AIBN, and the solution was deoxygenated by bubbling dry N_2 gas through it. It was then heated to 60°C for 30 minutes. The polymers which precipitated out of benzene were dissolved in THF and reprecipitated from CCl_4 twice, vacuum dried at 50°C, and stored in a descicator. A typical ^1H-NMR spectrum of the copolymer is shown in figure 1.

Conductometric titrations In a typical titration 0.04 g of the polymer was dissolved in 5 ml THF and 10 ml of 0.19 N NaOH was added to it and stirred to effect complete hydrolysis and neutralisation of the anhydride groups. The residual NaOH was then back titrated with 0.1N HCl. The composition of the copolymers thus determined is listed in table 1.

Table 1

Mole fraction of MAH in feed	% Yield	Mole fraction of MAH in the copolymer
0.9	15	0.56
0.75	42	0.53
0.50	75	0.52
0.25	26	0.52
0.10	19	0.49

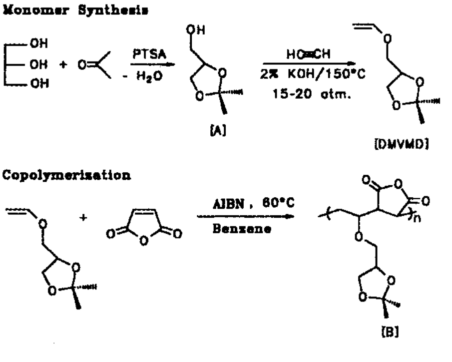
Crosslinking Studies Free standing films were cast by pouring a solution of the copolymer in THF into a silylated glass casting dish. The solvent was then allowed to evaporate slowly under a slow purge of dry N_2 gas to prevent premature crosslinking. Films (ca. 50 μm thickness) of the polymer were then placed in a closed chamber saturated with water vapour at ambient temperature and the IR spectrum of the films were recorded after periodic intervals.

Model reactions: Reaction (1) 2,2-Dimethyl 1,3 dioxolane (2 g, 0.0195 moles), acetic anhydride (5 g, 0.0489 moles) and water (0.351 g, 0.0195 moles) were refluxed for 24 h. The mixture was subject to fractional distillation to give ethylene glycol diacetate in 46% yield. B.P 55°C/1mm. The reaction was repeated using 0.1 eqv. of water per mole of 2,2-dimethyl-1,3-dioxolane to obtain ethylene glycol diacetate in a yield of 10%.

^1H NMR ($CDCl_3$): δ 2.08 (s,3H, $OCOCH_3$), δ 4.25 (S,2H,CH_2O).

Reaction (2) 2,2-dimethyl-1,3-dioxolane (2 g, 0.0195 moles), acetic anhydride (5 g, 0.0489 moles) and acetic acid (1.17 g, 0.0195 moles) were refluxed for 24 h. Attempted fractional distillation of the reaction mixture failed to yield any fraction corresponding to ethylene glycol diacetate.

RESULTS AND DISCUSSION



Scheme-1

The monomer, 2,2-dimethyl-4-vinyloxymethyl-1,3-dioxolane, was synthesized according to scheme 1. The direct high pressure vinylation of the isopropylidene glycerol, using acetylene gas and THF as a solvent in the presence of powdered KOH, gave good yields of the monomer. The monomer was easily purified by fractional distillation under reduced pressure. The ^{1}H-NMR spectrum of the monomer (Figure 1) was in accordance with the expected structure.

Copolymerisation of DMVMD with maleic anhydride (MAH) in a 1:1 ratio was carried out in benzene at 60°C using AIBN as the initiator. The polymer was insoluble in benzene and precipitated out of solution. The polymers were isolated, dissolved in THF and reprecipitated in CCl_4. Care was taken to use dry solvents to prevent premature hydrolysis of the anhydride which often lead to the formation of insoluble polymers. The ^{1}H-NMR spectrum of the polymer (Figure1) shows distinctly the presence of the gem-dimethyl protons of the ketal group. However, the peaks due to the backbone methylene and methine protons could not be unequivocally assigned to enable exact determination of the copolymer composition. Hence, the composition was determined using conductometric titration.[8]

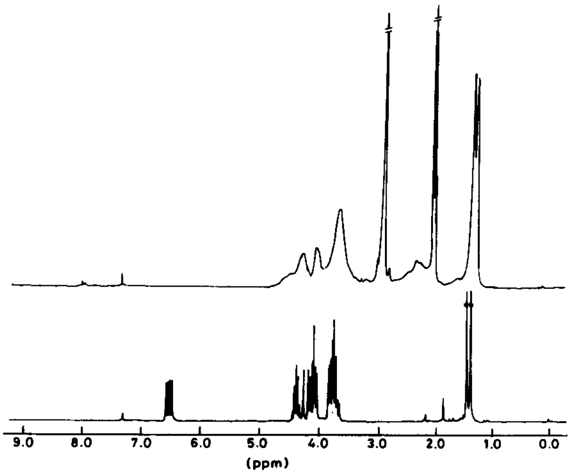


Figure1 ^{1}H-NMR spectra of the monomer in $CDCl_3$ (bottom) and the alternating copoylmer in acetone-d_6 (top).

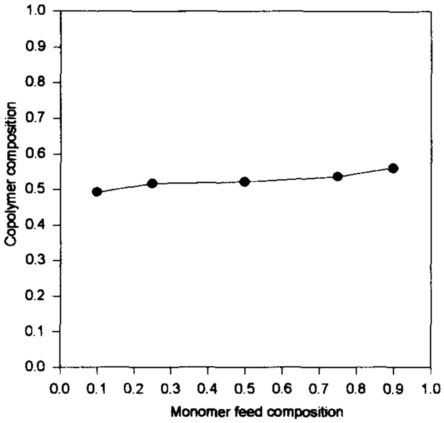


Figure 2 Plot of copolymer versus monomer feed composition.

In order to establish the alternating nature of the copolymer, copolymerisation starting with different mole ratios of the two monomers were carried out and the composition of the resulting copolymers were established. The results are given in table 1. A plot of the mole fraction of DMVMD in the feed versus that in the copolymer is shown in figure 2. It is clear that the composition of the copolymers in all cases is around 1:1, implying that the copolymerization is indeed strictly alternating, as expected. The ^{1}H-NMR spectra of all the copolymers were also found to be essentially identical.

The copolymers were found to be soluble in a vareity of solvents such as acetone, THF etc., and free standing films were easily solvent cast. In order to prevent premature crosslinking, care was taken to evaporate the solvent under a slow stream of dry N_2 gas. The solvent cast films became insoluble upon extended exposure to ambient atmospheric conditions. We speculated that, if chemical crosslinking were to occur, it may be catalyzed by moisture, which would generate carboxylic acid groups by the hydrolysis of the anhydride present in the polymer.

Crosslinking Studies

In order to establish the mechanism of crosslinking, free standing films of the alternating copolymer, of ca. 50μ thickness, were placed in a closed chamber saturated with water vapour at ambient temperature and its solubility and FT-IR spectra were followed with time. Figure 3 shows the FT-IR spectra of the nascent film and that after an 18 h exposure to water

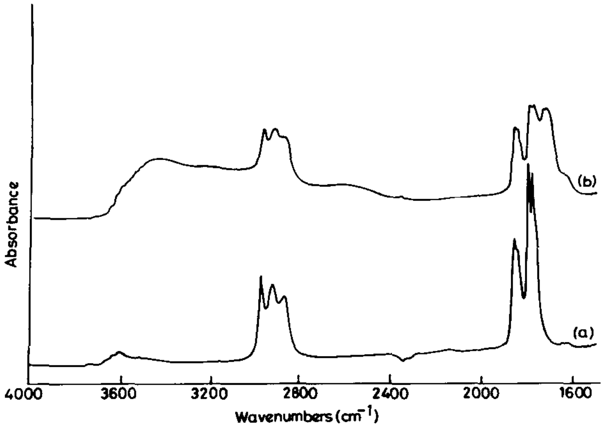
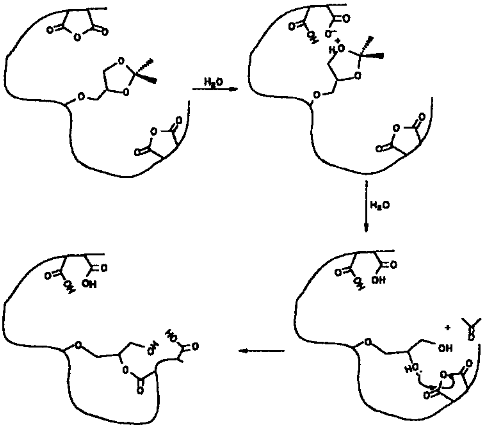


Figure 3 FT IR spectra of the nascent copolymer film (a) and after 18h exposure to saturated water vapour (b).



Scheme-2

vapour. At this stage the polymer film also becomes insoluble. Two distinct features in these spectra are noteworthy. First is the appearance of peaks around 1740-1760 cm-1, due to the formation of ester groups, that gradually gains in intensity at the cost of the anhydride peaks between 1860-1770cm-1. The second is the appearance of a broad peak at around 3400 cm-1, which can be attributed to -COOH groups resulting from the hydrolysis of anhydride in the presence of excess water. Based on these studies, we speculate that the ester crosslinks are formed by first hydrolysis of some of the anhydrides giving rise to carboxylic acid groups, which in turn catalyse the deprotection of the dimethyl ketal.[9] The resulting diol further reacts with the residual anhydride giving rise to the ester crosslinks. A schematic representation of the crosslinking process is shown in scheme 2.

In order to confim this hypothesis, a series of model reactions using acetic anhydride and 2,2-dimethyl-1,3-dioxolane were carried out. It was found that when equivalent amounts of dimethyl dioxolane and water were reacted with 2.5 fold excess of acetic anhydride, about 46% of the expected product, ethylene glycol diacetate, was isolated. However, upon reducing the amount of water to 0.1 equivalent (relative to the dioxolane) only about 10% of the product was obtained. Furthermore, when the reaction was carried out in the absence of water but in the presence of glacial acetic acid (the anhydride hydrolysis product) no product was formed. This confirms that both the hydrolysis of the ketal and the anhydride are processes that indeed occur simultaneously and compete for the water initially available in the system, and also that the hydrolysis of the ketal functionality preceeds the formation of the ester crosslinks. Preliminary IR spectral studies further appear to suggest that there may be an induction period before the cross-linking process begins. This may be due to the gradual diffusion of water molecules across the relatively hydrophobic surface of the nascent polymer. As the hydrolysis of the surface anhydride groups occur, the surface becomes more hydrophilic and the diffusion of water is facilitated and so also is the rate of cross-linking. Further studies of the kinetics of this process is currently in progress. Studies to vary the rate of crosslinking by terpolymerisation with both hydrophilic and hydrophobic comonomers are also currently underway.

CONCLUSIONS

A novel vinyl ether, DMVMD, has been synthesized from readily available starting materials, such as glycerol, acetone and acetylene. DMVMD forms an alternating copolymer with maleic anhydride which undergoes an interesting moisture-induced crosslinking reaction leading to the formation of ester crosslinks. The crosslinking reaction, we believe, proceeds by the initial hydrolysis of some anhydride groups leading to the generation of carboxylic acid groups which then catalyse the hydrolysis of the ketal moieties. The resulting diols in turn react with the residual anhydrides to give rise to the ester crosslinks. The postulated mechanism was substantiated based on direct FT-IR studies and also on some model reactions. The presence of both anhydride and acid sensitive protected diol groups in the same polymer, thus makes this polymer a potential candidate for moisture curable coatings.

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