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Grafting of bio-monomers

1. Cationic graft copolymerisation of cardanol using borontrifluoridediethyletherate onto cellulose

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Summary

Cardanol was grafted onto cellulose using borontrifluoridediethyl-etherate as carbocationic initiator. The graft yield of 15-25% was obtained within two hours without significant gelation of the monomer. Extensive water repellency was shown by Whatman No.1 filter paper after the grafting reaction.

Introduction

Grafting of vinyl monomers onto cellulose has been the subject of extensive studies during the last decade or two (1-4). Grafted cellulose copolymers have been found to have improved properties particularly in terms of water repellency, easyware characteristics, crease resistance, flame resistance, toughness etc. A study on the numerous reviews and articles on grafting of vinyl monomers onto cellulose indicates that one area that needs further input is the grafting of unsaturated bio-monomers isolated from plant materials. There exist a variety of bio-monomers having interesting structural features for incorporating speciality properties (5). Among these bio-monomers, cardanol (37330-39-5) obtained from the plant Anarcadium occidentale L.(6) has a variety of polymer applications and can be easily functionalised and polymerised cationically (7) into polymers with specific performance properties such as ion exchange, flame resistance (8-9) etc. The present communication reports the results of our work on grafting of cardanol onto cellulose by cationic mechanism. This will also be a case where instead of the usual short chain unsaturated monomers a long chain (C_{15}) unsaturated monomer with a phenolic functional group is grafted onto cellulose. This is significant because further chemical modifications at the hydroxyl group are possible.

Experimental

Materials

Cardanol was obtained by double vacuum distillation of cashewnut shell liquid (8007-24-7) at 3-4 mm Hg and the fraction distilling at 230-235 °C gave refractive index of 1.509 and Brookfield viscosity of 450-520 cps at 30 °C as reported for cardanol (10). Borontrifluoride-diethyletherate (48% BF_3, Fluka Chemicals Corporation, Germany) was used as supplied without further purification. Methylenechloride was a product of BDH and used after distillation. The experiments were carried out in nitrogen atmosphere at room temperature in a glove box.

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IR

The IR spectrum was recorded using a Perkin Elmer IR Spectrophotometer Model 882 and mull method was followed.

Scanning Electron Microscopy

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

Water repellency

The water repellency of the samples was measured by following methods such as the Sinking technique (1), water penetration test (11) and contact angle (12-13) measurements.

In Sinking method 1% of the wetting agent was used and measured at 30°C. Arsenezo-1 dye was used as the colour developing dye in the water penetration test. Contact angle of water droplets on the specimen was measured at 30°C with a travelling microscope with a crosshair eyepiece attached to a goniometer.

Typical grafting process

Sheets of Whatman's No.1 filter paper (1.5 x 12 cm) were used for this study. The sheets (batches of five) were immersed in borontrifluoridediethyletherate placed in screwcapped test tubes and allowed to interact for 1-2 hours at ambient temperature in a glove box. The paper strips were drained and dried in vacuo and then immersed in cardanol in a stoppered test tube for another three hours. The paper strips were then washed with acetone and Soxhlet extracted for 24 hours in acetone to remove homopolymer.

The degree of grafting (π) (14) was calculated using the formula

$$\pi = \frac{A - B}{B} \times 100$$

where A is the weight of the grafted sample after extraction and B is the weight of the original sample.

Results and Discussion

Effect of time on grafting percentage

Figure 1 shows the percentage grafting of cardanol with time of contact of borontrifluoridediethyletherate with the filter paper. There is an induction period upto 20 minitues after which only grafting reaction starts. A maximum percentage of 25 is reached in about 100 minutes and then no further improvement could be observed.

Effect of concentration of borontrifluoridediethyletherate

Figure 2 shows the effect of change of concentration of borontrifluoridediethyletherate using methylenechloride. The minimum concentration required for the graft copolymerization was 20% (vol/vol) $BF_3.OEt_2$ in methylenechloride. The percentage of grafting is only 8-9% upto a concentration of 70% (vol/vol) and then there is a steep increase in percentage of grafting to 25% at 80% (vol/vol) concentration of $BF_3.OEt_2$

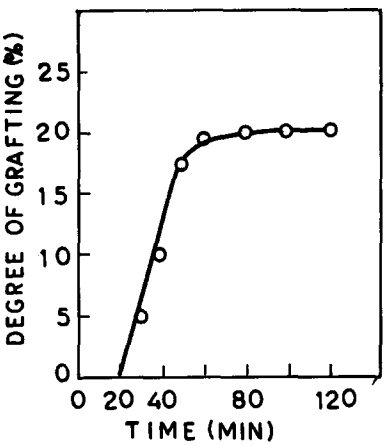


Fig. 1: Effect of time on percentage of grafting

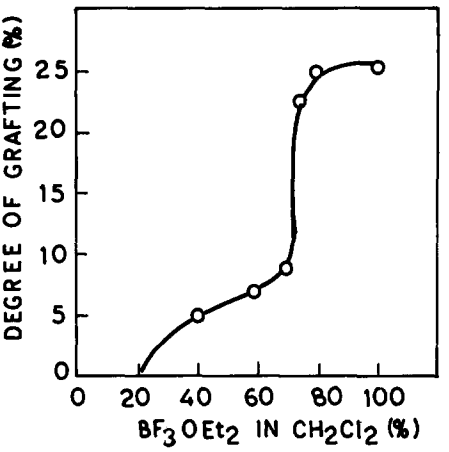


Fig. 2: Effect of concentration of $BF_3.OEt_2$ in CH_2Cl_2 (vol/vol) on percentage of grafting

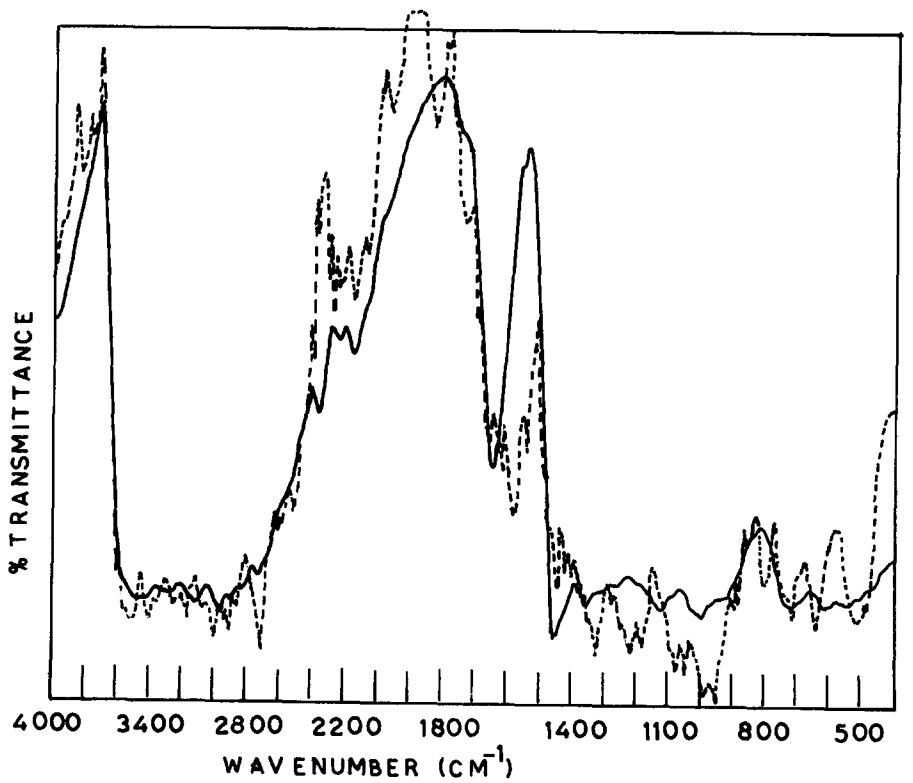


Fig. 3: IR spectrum of Whatman No.1 filter paper (——) and grafted paper(...)

in methylenechloride. It is possible that the active ionic species for effecting the grafting needs a critical concentration.

Figure 3 shows the IR spectrum of the original filter paper and the grafted paper. The spectrum gives additional peaks at 3000 cm^{-1}, 1600 cm^{-1} etc. showing the presence of aromatic structure in the sample. This indicates an evidence for grafting because the aromatic structure can come only from grafted cardanol.

The SEM pictures show that grafting has clearly taken place. Figure 6 shows grafted polymer existing as granules on the surface of cellulose whereas with extended period of grafting a neat film could be visible in Figure 7 in comparison to the ungrafted samples (Figures 4&5). Similar changes in SEM photograph of the treated samples have been reported (15). It took 1600 secondsfor the grafted sample with the extent of grafting from 15 to 20% to sink in water compared to 10 seconds for the untreated sample indicating excellent water repellent properties of the grafted sample.

In the water penetration test the untreated paper instantaneously develops red colour and the treated sample withstands more than 12 hours. The contact angle measurements gave as the contact angle larger than 90^{o}.

Fig.4: SEM photo of untreated paper

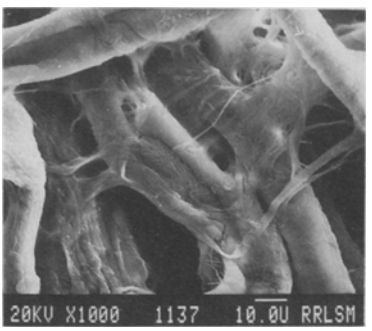


Fig. 5: SEM photo of $BF_3.OEt_2$ treated paper

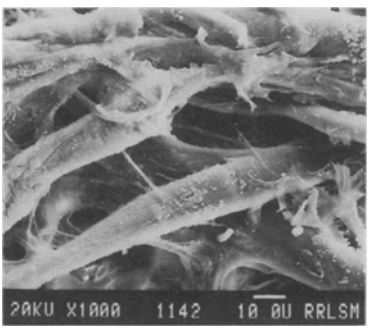


Fig. 6: SEM photo of grafted paper 1 hour reaction

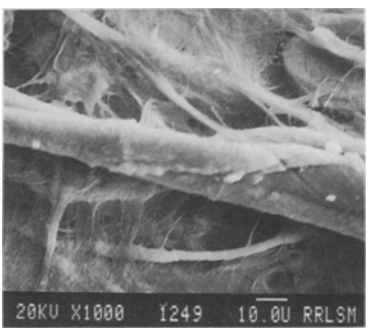
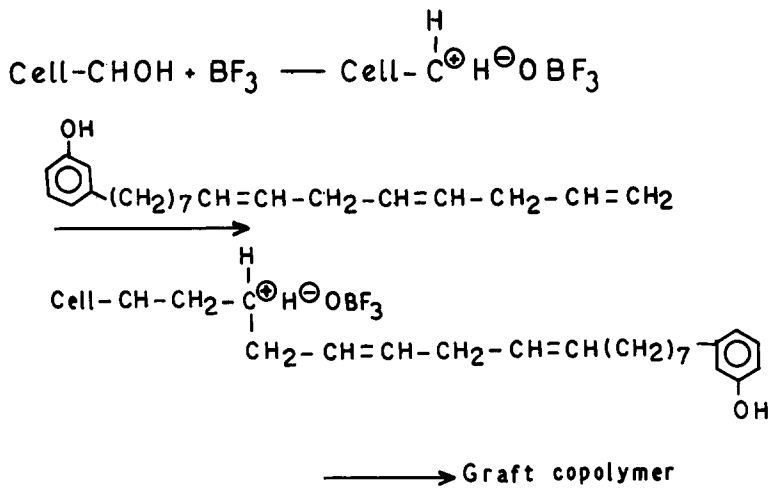


Fig. 7: SEM photo of grafted paper 2 hours reaction

Acid aging tests (15) with 70% sulphuric acid showed that the grafted paper has excellent acid resistance (16).

BF_3 a Lewis acid is known to interact with hydroxyl groups of cellulose which in actual practice serve as a Lewis base. The resultant Lewis salt will still be a catalyst, and can thus initiate polymerisation of a suitable monomer (11) as, for instance, cardanol. Taking for example, the triene component of cardanol which is having a terminal double bond, the graft copolymerisation can be represented as follows:



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