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Photo-induced graft copolymerization of methyl methacrylate onto cellulose containing benzoyl xanthate chromophore*

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Summary

Cellulose is conveniently functionalized to the corresponding S-benzoyl cellulose xanthate. Photolysis of S-benzoyl cellulose xanthate in presence of methyl methacrylate (MMA) initiated graft copolymerization which was confirmed by different analytical techniques.

Introduction

Photo-induced graft copolymerization of vinyl monomers onto cellulose has been a subject of intense activity during the past two decades[1-3]. Compared with other methods of grafting of vinyl monomers by free radical polymerization, this method has many advantages such as the controlled generation of radical sites on cellulose and a higher grafting efficiency[4-7]. In photo-induced graft copolymerization, certain photocleavable chromophores such as N,N-Diethyldithiocarbamate and phenyl sulphide groups are used for the grafting reaction[8-11]. Recently it has been shown in this laboratory that photolabile xanthate chromophore can be used to initiate grafting of acrylic monomers onto polystyrene beads[12]. A serious limitation of this method however has been that the initiator moiety absorbs below 300 nm, where most of the monomers also have absorption and thereby enhancing the formation of homopolymers. However, the use of aroyl xanthates as photoinitiator overcomes this limitation and found to be useful for the photocrosslinking and photopolymerization studies[13-14]. It is well known that xanthate group can easily be incorporated into cellulose and we have found that S-benzoyl cellulose xanthate is photocleavable under UV irradiation. In this paper, we report the photo-induced graft copolymerization of methyl methacrylate (MMA) onto cellulose using benzoyl xanthate chromophore as the functional group.

Experimental

Sheets of Whatman's No.41 filter paper were used as the starting cellulosic material for the preparation of sodium cellulose xanthate. MMA was washed with 10% aqueous sodium hydroxide, dried over anhydrous sodium sulphate and distilled under reduced pressure. Solvents were purified and distilled before use.

Photoirradiations were carried out on an Oriel Optical Illuminator, equipped with 500 W super high pressure mercury lamp (USHIO USH 508 SA). IR spectra were recorded on a Perkin-Elmer Model 882

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spectrophotometer and the SEM pictures were taken on a JEOL JSM-35 C scanning electron microscope. X-ray diffraction patterns were obtained from a Philips PW-1710 powder diffractometer using Cu-K$_\alpha$ radiation. Thermogravimetric analyses were carried out using a Du Pont 951 TGA, attached to a Du Pont 2000 thermal analyst system. GPC analyses were carried out using a Hewlet-Packard 1081 B HPLC, after calibration with standard polystyrene samples.

Preparation of Sodium Cellulose Xanthate

Chopped filter papers (Whatman No.41, 10 g) and aqueous sodium hydroxide solution (18%, 100 mL) were mechanically stirred for 2 h, followed by the addition of carbon disulfide (10 mL). The reaction mixture was stirred for an additional 3 h and the contents were poured into excess of methanol. The precipitated sodium cellulose xanthate was washed with cold methanol and dried under vacuum. IR (KBr); 1220 cm^{-1} (C=S).

Preparation of S-Benzoyl Cellulose Xanthate

To a solution of benzoyl chloride (5 mL) in dichloromethane (20 mL), sodium cellulose xanthate (2 g) was slowly added with constant stirring. The stirring was continued for an additional period of 2 h and the yellow S-benzoyl cellulose xanthate that formed was filtered, washed with dichloromethane, water and acetone and dried under vacuum. IR (KBr); 1720 (C=O), 1220 (C=S), and 1050 cm^{-1} (C-O).

Photografting of MMA: General Procedure

A mixture of S-benzoyl cellulose xanthate (3) (1 g) and MMA (2 mL) was suspended in a pyrex vessel containing 50 mL of distilled water. The reaction mixture was degassed for 10 min with argon and irradiated for known periods of time. The grafted polymer was collected by filtration, dried and extracted with chloroform for 12 h, using a Soxhlet apparatus. After extraction, the grafted cellulose was collected and dried in a vacuum oven at 60^{0} C. The homopolymer of MMA was obtained by pouring the concentrated chloroform extract in excess of methanol. The percentage grafting (G) and the graft efficiency (GE) were calculated from the change in weight of cellulose on grafting and weight of homopolymer.

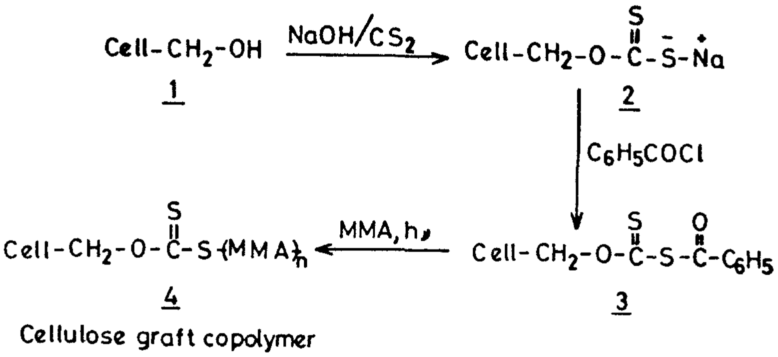
Results and Discussion

Preparation of S-Benzoyl Cellulose Xanthate (3)

The sodium salt of cellulose xanthate was prepared according to a reported procedure[15]. The sodium salt on further reaction with benzoyl chloride gave the corresponding S-benzoyl cellulose xanthate (3) (Scheme 1). The IR spectrum of (3) showed absorption bands at 1720 (C=O), 1220 (C=S) and 1050 cm^{-1} (C-O).

Photografting of MMA onto S-Benzoyl Cellulose Xanthate (3)

Photografting of MMA onto the cellulose xanthate (3) was carried out in different solvents under identical photolytic conditions (Scheme 1).



Scheme 1

Among the different solvents tried, water and methanol gave maximum efficiency for grafting. As mentioned in the experimental section, instead of adding the monomer directly into the suspension of the cellulose xanthate (3) in water or methanol, a pre-soaking procedure was adopted. This procedure has a profound effect on the efficiency of grafting as compared to the direct addition of the monomer. Since methanol and water are non-solvents for MMA, high local concentrations and intimate contact of the monomer with the photoinitiator moiety of the cellulose matrix are achieved. This must have enhanced the efficiency of photoinitiation and the subsequent termination of the growing PMMA chains by the thiocarbonyl thiyl radicals of the cellulose, which in turn, improve the efficiency of grafting. This is in agreement with the earlier reports by Imoto[16] and Takahashi et al[4,5] which explain the enhanced graft efficiency of MMA onto cellulose when carried out in aqueous system.

Figure 1 shows the relationship between the graft efficiency and the irradiation time. The graft efficiency was found to increase to a certain extent and then gradually decrease with increased irradiation time. This could be due to the increased formation of the homopolymer,

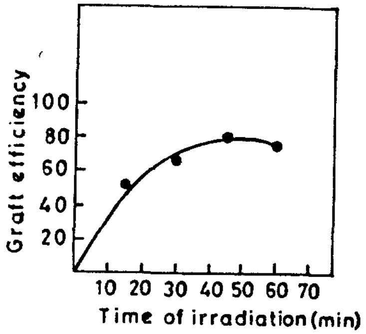


Figure 1: Relationship between the graft efficiency and the time of irradiation

arising due to prolonged irradiation. The grafted PMMA chains were isolated from the cellulose backbone by treating them with 72% sulphuric acid and the resultant polymers were analysed by GPC. The GPC analysis of the grafted PMMA chains did not show any significant change in their molecular weights. This observation suggests that the irradiation time does not have much influence on the molecular weights of the grafted PMMA chains. This is in agreement with a recent report on the photopolymerization studies of MMA using aroyl xanthate as photoinitiator[14].

Evidence for the Grafting of MMA

The photoinduced grafting of MMA onto the cellulose xanthate (3) was confirmed by several analytical techniques. The IR spectrum of the grafted cellulose showed the presence of characteristic ester absorptions of PMMA at 1737 cm^{-1}. The PMMA chains were isolated from the grafted cellulose and compared with authentic samples of PMMA., The IR spectra are found to be identical in both the cases.

Further confirmation of the grafting of MMA onto the cellulose xanthate (3) was obtained from comparative studies of the scanning electron microscope (SEM) pictures of the ungrafted and grafted cellulose. The SEM picture of the ungrafted cellulose at magnification X 1000 is shown in Figure 2(a), which indicates a nearly smooth surface. Figure 2(b) is the SEM picture of the MMA-grafted cellulose at magnification X 1000. This picture clearly indicates the presence of grafted PMMA chains on the surface of the cellulose fibres. The space between different fibres have been filled by grafted PMMA.

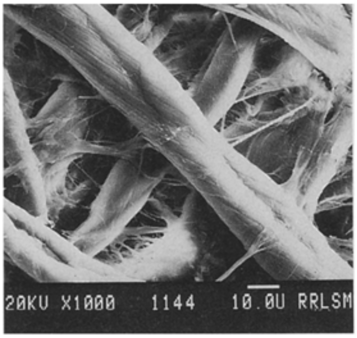


Figure 2(a): SEM photograph of ungrafted cellulose

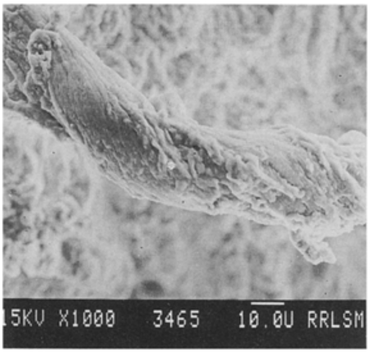


Figure 2(b): SEM photograph of PMMA grafted cellulose

Thermogravimetric analysis (TGA) of the ungrafted and grafted cellulose (Figure 3) indicates that the initial decomposition temperature (Ti) of the former is lower (240°C) than that of the latter (296°C, 120% grafting). This enhancement in Ti with the increase in the percentage grafting is an additional evidence for the grafting of MMA onto the cellulose xanthate (3).

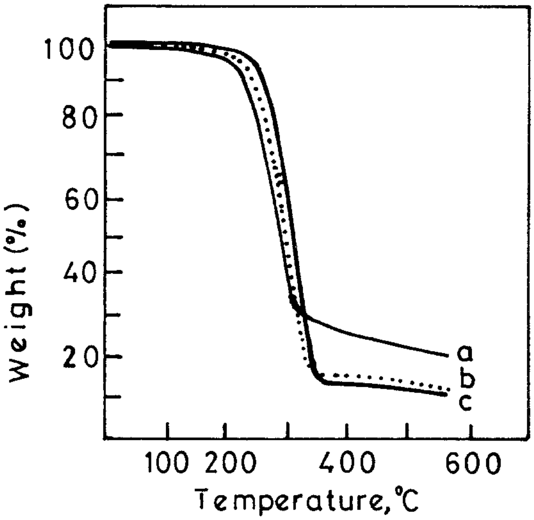


Figure 3: TG curves of (a) S-benzoyl cellulose xanthate, (b) 50% PMMA grafted and (c) 120% PMMA grafted.

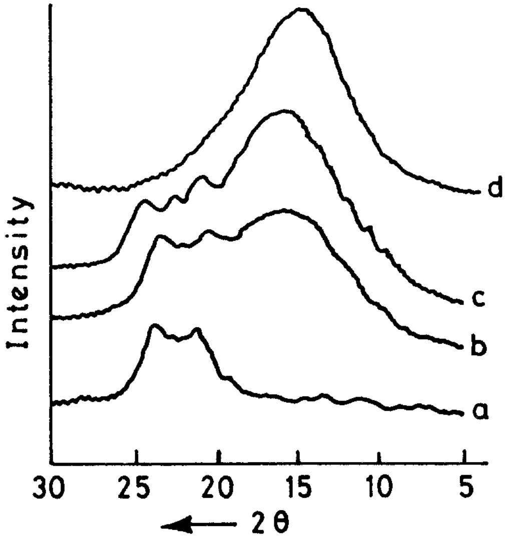


Figure 4: XRD patterns of (a) S-benzoyl cellulose xanthate, (b) 50% PMMA grafted, (c) 120% PMMA grafted and (d) pure PMMA.

In Figure 4, the X-ray diffraction (XRD) patterns of the ungrafted and PMMA-grafted cellulose are compared with that of pure PMMA. From the XRD patterns, it is clear that the peak corresponding to PMMA ($2\theta = 10$ to 18^0) increases with increase in the percentage grafting.

Mechanism of Photografting

Aroyl xanthates are known to undergo homolytic scission of the C(=O)-S bond, generating benzoyl and thiocarbonyl thiyl radicals[17]. Aroryl xanthates and their polymeric analogues have been used for several applications in polymer chemistry[9, 10]. Based on analogy to earlier reports, we infer that the S-benzoyl cellulose xanthate (3) undergoes an analogous photocleavage, generating the thiocarbonyl thiyl radicals on the cellulose and benzoyl radicals in solution. The polymerization of MMA is initiated by the benzoyl radicals and terminated by the thiocarbonyl thiyl radicals present on cellulose, eventually leading to the grafting of MMA.

Conclusion

The incorporation of the benzoyl xanthate chromophore on cellulose facilitates the photochemical generation of free radical centres which subsequently initiate the graft polymerization of MMA. This method provides an easy procedure to incorporate high percentage of PMMA onto cellulose and has the potential for making biodegradable polymers.

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