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The Photochemically-Induced Grafting of Styrene onto Cellulose in the Homogeneous Styrene/Cellulose/ D.M.S.O./HCHO System

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Synopsis

Styrene has been successfully grafted onto cotton cellulose under 'homogeneous' conditions provided by initial methylolation using the cellulose/DMSO/HCHO system. The attendant homopolymerization reaction has also been examined. Both grafting and homopolymerization show a rapid initial rate which appears to level off. The homopolymerization reaction increases with increasing concentration of styrene in the medium. Grafting is seen to maximize with increasing bulk monomer concentration, the position of the maximum showing some dependence on the exposure time, under otherwise standard conditions. These observations are interpreted in terms of increasingly restricted access of the monomer into the substrate, arising from the grafting process, which reduces the level of solubility of the methylol cellulose-polystyrene graft copolymer entity.

Introduction

The methylol cellulose (cellulose/DMSO/HCHO) system, as a means of cellulose solution, is now reasonably well established [1-3]. This procedure has been used as a preliminary to cellulose regeneration and derivitivization. Significant advantages of such a system include the ease of handling, the considerable storage life of solutions and the prospect of greater homogeneity of product modification resulting from the fact that reactions are completed in solution. Here we wish to report our observations on the photochemically induced grafting of styrene onto methylol cellulose in dimethylsulfoxide (DMSO). We shall concentrate on certain kinetic features while observations associated with the physical characterization of products will be reserved for later publication. Much work has been devoted to studies of grafting to cellulosics under heterogeneous conditions [4-6]. Solution grafting onto cellulose has been largely neglected owing to the non-availability of suitable media for grafting which would permit regeneration of the cellulose on completion of the grafting process. The development of the cellulose/DMSO/HCHO system [1,2] and related media (e.g. cellulose/DMF/N_2O_4)[3] has opened up new approaches to cellulose modification through grafting.

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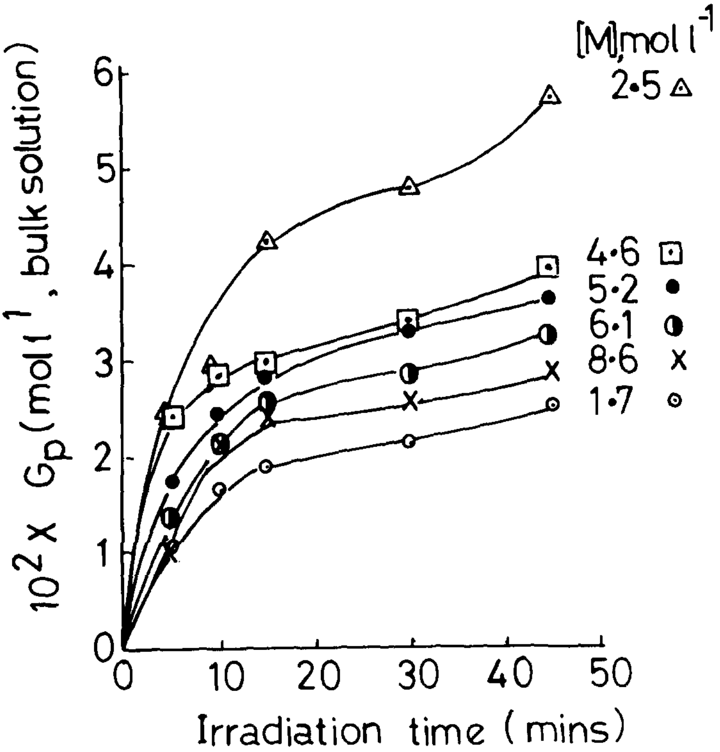

Figure 1. Variation in extent of grafting with irradiation time for monomer concentrations in the bulk phase of ○, 1.7; △, 2.5; □, 4.6; ● 5.2; ◑ , 6.1 and x, 8.6 mol/l of bulk phase respectively.

Experimental

Cellulose methylolation was a modification of the procedure given by Johnson et al [1] and has been fully reported by Guthrie and Hardcastle[2]. Cellulose (cotton wool), DMSO and paraformaldehyde. (1 : 100 : 5 parts by weight) were heated under reflux at 393 K (± 5 K) for 8 hours, though a clear solution was obtained after only 1 hour. The solution so prepared was stable during the duration of the study as shown by regular dynamic viscometric measurements taken on a Haake Rotovisco rotary viscometer at 303 K over various shear rates. The concentration of methylol cellulose in the parent solution was determined by precipitation of known volumes of methylol cellulose in DMSO into a 20 times excess of methanol. The precipitate was allowed to form overnight before filtering on No. 4 porosity sintered crucibles and drying to constant weight at 313 K under vacuum. To provide a guide to the level of consistency each determination of this type was repeated 5 fold.

Photoinitiation procedures

The concentrations of the photoinitiator (2-chlorothioxanthone) and the synergist (dimethylaminoethanol) were kept constant at the start of each grafting run (0.50% and 0.50% by weight respectively of the methylol cellulose/DMSO/HCHO solution). The relevant densities are styrene, 0.904g cm^{-3}; synergist, 0.887g cm^{-3} and the methylol cellulose solution, 1.251g cm^{-3}. Styrene was then added in such a way as to provide a series of 6 bulk solutions containing the monomer in a range of concentrations of 1.73, 2.46, 4.36, 5.16, 6.17 and 8.62 x 10^{-2} mol of styrene per l of bulk solution.

Irradiation was carried out for intervals of 5, 10, 15, 30 and 45 minutes for each monomer concentration, using a 125W PRIMARC medium pressure U.V. lamp, care being taken to ensure that heating of the grafting medium did not occur and that each solution was continuously agitated during exposure. Sample assembly consisted of the centrally mounted source surrounded by a silica envelope designed to permit cooling from an external water source. The grafting medium was held in a pyrex photochemical reactor into which the cooled lamp was assembled. Agitation was provided by a magnetic spiggot. Grafting and homopolymerization reactions were undertaken at 313 K, maintained from an external thermostirrer control.

On completion of irradiation, the bulk solution and any precipitated polymer were transferred to a 3 fold excess of chilled methanol when precipitation of polystyrene homopolymer and the graft copolymer took place. Thorough washing with methanol, to remove unpolymerized styrene and residual DMSO, followed filtration of

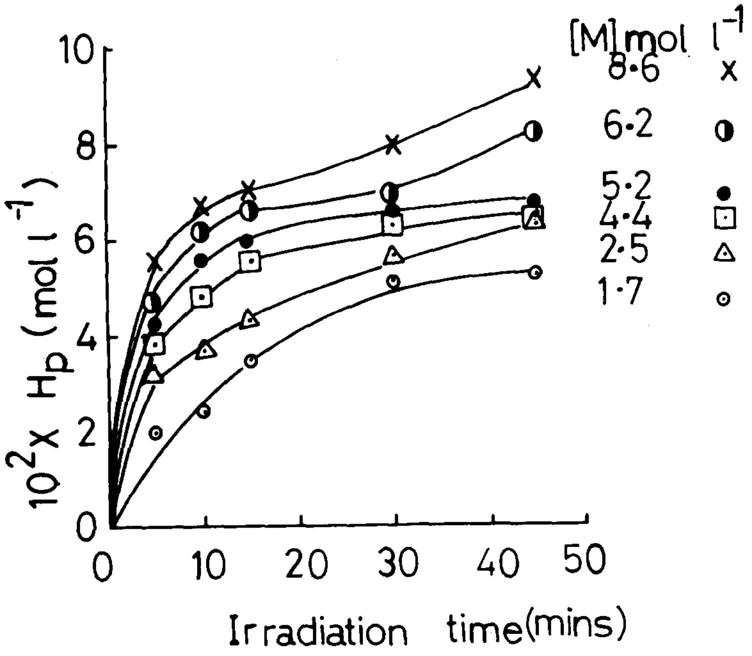

Figure 2. Variation in the extent of homopolymerization with irradiation time for monomer concentrations of ⊙, 1.7; Δ, 2.5; ☐, 4.6; ●, 5.2; ◑, 6.2; x, 8.6.

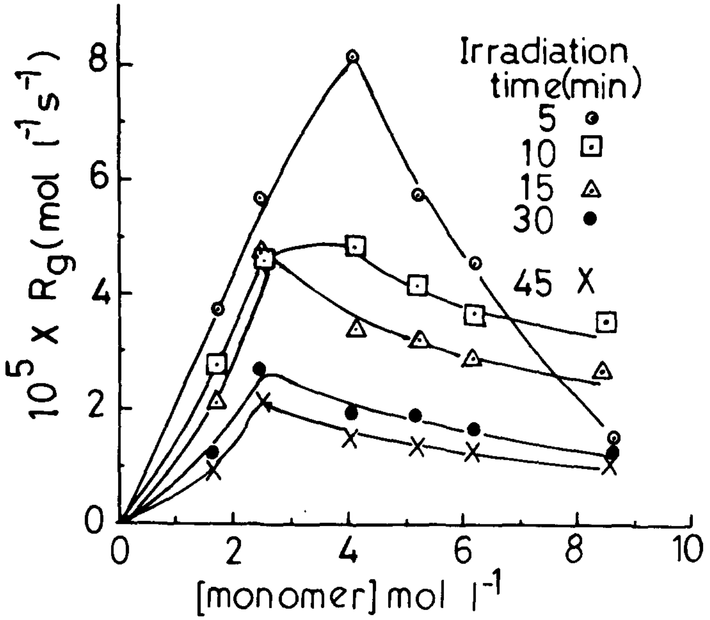

Figure 3. Variation in the rate of grafting, R_g , with monomer concentration.

insoluble material on porosity 4 sintered crucibles. Polystyrene homopolymer was removed from the residues by extraction, on a Soxhlet extractor using a tetrahydrofuran/water (98:2) mixture, for 6 hours. The homopolymer was obtained by precipitation of the extract in methanol (chilled). The cellulose graft copolymer and the polystyrene homopolymer were then isolated and dried to constant weight as described previously. While it is realized that this type of procedure can lead to difficulties (e.g. fractionation phenomena), the use of duplicates at each stage ensured a satisfactory level of consistency throughout.

Results and Discussion

Assay of the methylol cellulose solution used in this work gave 5.29 g of methylol cellulose/l of polymerizing medium. (The deviation in determination was in the range 5.27 to 5.31 g l^{-1}). This value is used in calculations of grafting yields and grafting rates. Since the grafting medium is apparently homogeneous throughout, the grafting rates can be expressed adequately in mol of styrene grafted/l of bulk solution/sec. A similar procedure is used for the homopolymerization reactions. This approach is facilitated by use of a constant volume (20cm^3) of grafting medium throughout.

Figures 1 and 2 show the increase in grafting and homopolymerization, respectively, with increasing irradiation time for the various initial monomer concentrations. While the homopolymerization process appears to be reasonably straight forward, the grafting reaction is complicated by the presence of maxima which maximize at an initial monomer concentration of 4.36 mol of styrene l^{-1} of bulk solution. These maxima are perhaps best shown by plotting the change in the overall rate of grafting against the original bulk monomer concentration (Figure 3) for each of the irradiation periods covered. Figure 3 presents some interesting features. The occurrence of maxima in studies of grafting patterns have been observed previously.(7-9.). They are often associated with Trommsdorff type phenomena or where precipitation of polymer follows as a consequence of the polymerization reaction. In this study the situation is somewhat more complex in that there is little change in the viscosity of the medium as a result of grafting, as shown by dynamic viscosity studies, the reaction always being carried out to low conversion levels. Also, these deviations from expected behaviour are not restricted to extended conversion but apply throughout each kinetic run. One possibility is that the addition of monomer to the bulk medium brings about changes in the morphology of the methylol cellulose in the dimethyl sulfoxide. One may propose that an open 'gel-like' phase is formed which contains trapped monomer as well as the photoinitiator and synergist. Should initiation take place within these transparent 'gels', polymerization would proceed until monomer depletion occurs. An open 'gel phase' would be supported to an upper limit in the monomer concentration (a non-solvent as far as the methylol cellulose/DMSO is concerned) during which the tendency towards reduced grafting, arising from 'gel' compaction, is more than compensated for by the higher monomer concentration within the loosely structured 'gel'. At a critical monomer concentration, the methylol cellulose/DMSO/Styrene medium acquires a more rigid form in which methylol cellulose/DMSO domains are produced owing to preferential adsorption of the DMSO as the styrene concentration is increased. The transport of styrene from the exterior to the interior of such domains might now become diffusion controlled as a result of the increase in the heterogeneity of the system arising from increases in the bulk monomer (non-solvent) concentration. It is proposed that rheological studies to be carried out to examine these points further.

Similar reasoning could be put forward for the role of the synergist and photoinitiator. Since the concentration of each of these was held constant throughout this study we feel that their contribution to the abnormal behaviour is relatively minor. However, an alternative possible cause of this type of behaviour might arise from a decrease in the number of grafting sites as the monomer/solvent ratio is changed. There is a possibility that addition of styrene to the methylol cellulose/DMSO causes partition of the initiator/synergist system away from the vicinity of the methylol cellulose leading to a decrease in the number of available grafting sites. More detailed studies are being carried out on this type of system aimed at an understanding of the detailed mechanism of the grafting process. These results will be made available in due course. It is reasonably certain that the physical nature of this system is much more complicated than that normally encountered in 'true solution' grafting(10-12).

Acknowledgement:-

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