

# Sensitized Photoinitiated Grafting of *N*-Vinyl-2-Pyrrolidone (NVP) to Woolen Substrates\*

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## Synopsis

The photoinitiated copolymerization of *N*-vinyl pyrrolidone onto woolen substrates from aqueous solutions has been studied. A novel water-soluble photosensitizer, 4-(sulfomethyl) benzil sodium salt (Quantacure SKS—patent pending), has been developed and its efficiency assessed with and without an amine synergist. The initiator is nonmutagenic within the terms of the Ames testing procedure. Induction periods were not observed. The action of the so-called synergist, dimethylaminoethanol, was to reduce or stop the grafting reaction. The significance of the pH of the aqueous medium is shown by a maximum in grafting being observed at pH = 4.0 for otherwise standard conditions. Aspects of impregnation procedure were examined, marked improvements in the grafting level being achieved by use of preliminary evacuation—freeze/thaw cycles.

## INTRODUCTION

Interest has been shown recently in the unsensitized and sensitized photoinitiated grafting of vinyl or acrylic monomers onto a variety of substrates.<sup>2-6</sup> Emphasis had rightly been placed on efficient rapid copolymerization, usually from solvent-based media. Such work is assisted by the supporting technology which exists in this area, particularly in surface coating, and also because non-aqueous systems are generally easier to work with than are the corresponding aqueous systems. One severe difficulty with water-based photocuring reactions lies in the much reduced activity of conventional photoinitiators when placed in aqueous solutions. This fact, coupled with their inherently poorer solubility, means that many of the accepted photoinitiator assemblies have little to offer photopolymerization reactions carried out in aqueous media. The situation is further complicated by the fact that enhancement of the aqueous solubility of photoinitiators, using substituted solubilizing groups, often leads to a further reduction in their photosensitizing ability.

Our interest lies in the synthesis and evaluation of specifically designed, water-soluble photoinitiators, particularly with regard to graft copolymerization reactions. Other procedures, which might benefit from the availability of such initiators, include aqueous dispersion coating, water-based printing processes, immobilization of reagents, and so on.

*N*-Vinyl pyrrolidone is of interest to copolymerization studies because of its low toxicity coupled with its ease of copolymerization with other acrylates. It has been reported that NVP generally improves the flexibility of substrates to which it is cured.<sup>7</sup> Another, long-term interest lies in grafting reactions involving

\* For details of the Ames testing procedure, see ref. 1.

mixed-monomer systems containing NVP, since it has been shown to be a positive synergist in copolymerization involving acrylate monomers. Morel, Jozefonvicz, and Aptel have shown that NVP, grafted onto various film types, provides for a series of effective, interesting pervaporation membranes operating through preferential adsorption, by the NVP grafted branches, of particular components of mixed-solvent systems.<sup>8</sup> We hope to extend this approach to studies of preferential adsorption by NVP grafted onto natural polymeric substrates with a view to improving the efficiency of action in terms of dyeability, ion-exchange properties, and enzyme immobilization.

Here we are concerned with the nature and lifetimes of the reactive species, factors associated with substrate preparation, the role of the photoinitiator and synergist, the pH dependence of grafting, the grafting rate profile, and efficient use of available monomer.

## EXPERIMENTAL

The monomer (NVP), was supplied as analytical quality and was purified by standard procedures. The "synergist," dimethylaminoethanol (DMAE), was used as supplied by the Aldrich Chemical Co. The photoinitiator used in this work was prepared as follows.

4-Methyl benzil was obtained via the Friedel-Crafts addition of toluene to phenylacetyl chloride and the conversion of the resultant desoxybenzoin by treatment with bromine and dimethylsulfoxide. 4-Methyl benzil was then converted to 4-(bromomethyl) benzil via the method of Krieg and Manecke,<sup>9</sup> using a mixture of *N*-bromosuccinimide and benzoyl peroxide under a 2-hr reflux (58.5% yield). The desired photoinitiator, 4-(sulfomethyl) benzil sodium salt, was obtained by overnight reflux of 4-(bromomethyl) benzil with sodium sulfite in an ethanol/water solvent. The solvent was stripped off by rotary evaporation and the product recrystallized from hot methanol, (yield 75.5%,  $\lambda_{\max} = 268$  nm, mp = 543 K). The solubility of 4-(sulfomethyl) benzil sodium salt in solutions of NVP in water of various compositions was determined in advance of polymerization studies. The photoinitiator was found to be soluble in the required concentration range.

We found that the 4-(sulfomethyl) benzil sodium salt is not mutagenic to salmonella typhimurium strains TA 98, TA 100, TA 1535, and TA 1538 in either the presence or absence of S9 homogenate when tested in either the presence or absence of daylight.<sup>10</sup> For convenience, the photoinitiator is coded SKS.

### Prepolymerization Procedures

The aqueous solutions of NVP were prepared at the 10% (w/v) level, except for studies of the influence of padding for which a 20% (w/v) NVP solution was used. Unbuffered solutions below pH = 7 were formulated in distilled water and adjusted to the required pH using perchloric acid. Buffered solutions were assembled in the required medium.<sup>11</sup> Tared (constant weight), conditioned (66% RH, 293 K) wool samples were treated to particular monomer compositions in sealed tubes and warmed to 323 K for 1 hr. The pieces were then carefully padded to a uniform weight by compression under known, controlled pressures to remove surplus solution. They were then placed in previously weighed, seal-

able polythene bags and the whole reweighed. Variations to this wool preparation took two forms: (1) no padding to uniform weight and (2) the application of vacuum, freeze/thaw cycles to the impregnated wool. The aqueous monomer solutions contained some or all of the following, depending on the parameter being investigated: monomer, synergist, photoinitiator, and pH modifier.

### Polymerization Procedures

Irradiation of the impregnated wool was achieved using a Primarc medium-pressure mercury lamp, centrally mounted in a rotating rig designed to ensure even exposure at a uniform distance from the lamp.<sup>2</sup> Exposure times were in a range up to 2 hr. The irradiated samples were reweighed, then extracted with water for 24 hr to remove occluded homopolymer. After extraction, the samples were air dried, then conditioned as before. The aforementioned evacuation/freeze thaw procedure<sup>12</sup> was followed by the sealing of ampoules under liquid nitrogen at  $1.33 \times 10^{-2} \text{ N m}^{-2}$ . The sealed ampoules were warmed to 323 K for 1 hr and the wool was then treated as before.

### RESULTS

The extent of grafting may be considered in two ways.

$$\% \text{ graft} = ((W_f - W_i^c)/W_i^c) \times 100 \quad (1)$$

where  $W_i^c$  is the initial weight of the woolen substrate after correction for any change in the weight of unmodified blanks and  $W_f$  is the weight of dried wool after irradiation.

$$\% \text{ graft} = \left[ \frac{(W_f - W_i^c)}{(W_w - W_i^c) \times [M]} \right] \times 100 \quad (2)$$

where  $W_w$  is the wet weight of wool after impregnation and padding.  $[M]$  is the monomer concentration [% (w/v) of the bulk solution].

Equation (1) gives grafting based on the original wool weight while eq. (2) expresses the grafting in terms of the apparent monomer available for grafting. In general eq. (2) provides a clearer picture of grafting characteristics in terms of efficient utilization of monomer. However, eq. (2) contains the built-in assumption that the concentration of monomer in the wool is identical to that in the bulk solution. We have evidence to suggest that this assumption is not fully justified. However, the level of deviation increases with increasing bulk monomer concentration. For solutions of 10% (w/v) NVP or less, such deviations are of low magnitude.

### Influence of pH on Grafting

Grafting was carried out on wool samples impregnated using aqueous NVP solutions in the range  $\text{pH} = 2\text{--}12$ . Figure 1 gives the extent of grafting achieved after 60-min irradiation at different pH values. No synergist was used and the monomer concentration of the bulk medium was maintained at 10% (w/v). A maximum is clearly seen at  $\text{pH} = 4.0$ . Generally, the initial rate of grafting decreased with increasing pH from  $\text{pH} = 2\text{--}8$ . However, the ultimate graft level

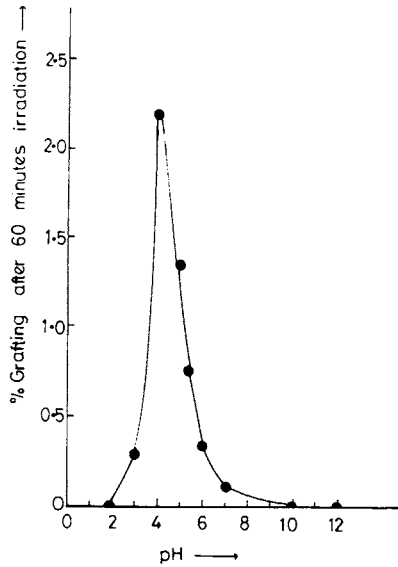


Fig. 1. Variation in % grafting (based on initial, corrected wool weight), with pH of bulk medium. Monomer concentration, 10% (w/v); initiator concentration, 0.5% (w/v).

was as shown in Figure 1. Wool is known to be activated towards grafting at low pH values. However, the lack of grafting at  $\text{pH} < 3$  may be explained by the decrease in the effective monomer concentration at such pH values. NVP is known to undergo rapid hydrolysis to acetaldehyde and pyrrolidone under acid conditions. This hydrolysis is enhanced at elevated temperatures, though it is also dependent on the acid used.<sup>13</sup> Thus, on reducing the pH, the monomer concentration becomes time dependent with respect to the bulk medium. An examination of blanking procedures to provide  $W_i^c$  has shown that the increase in weight of blanks increases with decreasing pH suggesting that the hydrolysis products combine with the wool. These hydrolysis products have been shown to be acetaldehyde and pyrrolidone, which may combine with wool under acid conditions at the impregnation temperature. This point is to be examined in detail. The lack of grafting at high pH values may be explained by the deactivation of the NVP under such conditions, NVP polymerization being inhibited by alkaline conditions.

### Aspects of Impregnation

The influence of padding on the grafting reaction was assessed using 20% (w/v) NVP, 0.5% (w/v), SKS and a buffered aqueous medium at  $\text{pH} = 6.0$ . Figure 2 shows the effect of padding on the extent of grafting, expressed as a function of the monomer which is ultimately converted to grafted NVP and on the basis of the weight of wool used. It is clearly seen that the padding operation greatly improves the utilization of the available monomer. However, expression of the level of grafting as a function of the weight of the wool taken, shows that the unpadded wool gives the highest graft. This is simply because the nonpadded system provides more monomer in solution for the grafting process. On padding, the monomer is forced into closer proximity with the substrate and consequently

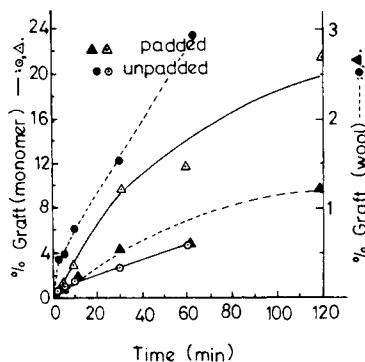


Fig. 2. Variation of % graft, based on wool weight (●, ▲) and monomer grafted (○, △) for padded (△, ▲) and unpadded (○, ●) systems, with time. Monomer concentration 20% (w/v); initiator concentration, 0.5% (w/v). Grafting carried out at pH = 6.0.

is more likely to be involved in grafting rather than in involuntary homopolymerization.

This point is made more significant by supporting studies of the relationship between the photoinitiator, SKS, the synergist, and the wool. As can be seen from Figure 3, the synergist dimethylaminoethanol, invariably reduces or inhibits the grafting reaction. Also it has been shown that SKS binds very strongly to the woolen substrate. Hence, the padding operation encourages close contact between the wool/SKS composite.

Figure 3 also shows the variation in level of grafting with time of irradiation for wool samples previously treated to freeze/thaw evacuation cycles. A 10% (w/v) NVP solution was used containing 0.5% (w/v) SKS. Experiments were carried out both with and without the 'synergist' dimethylaminoethanol, DMAE. The aqueous monomer solution was used at pH = 2. It has been shown that this low pH value gives no grafting under standard conditions. On the application of vacuum treatment, the monomer is brought into closer contact with the substrate and the photoinitiator. As can be seen, grafting occurs when vacuum

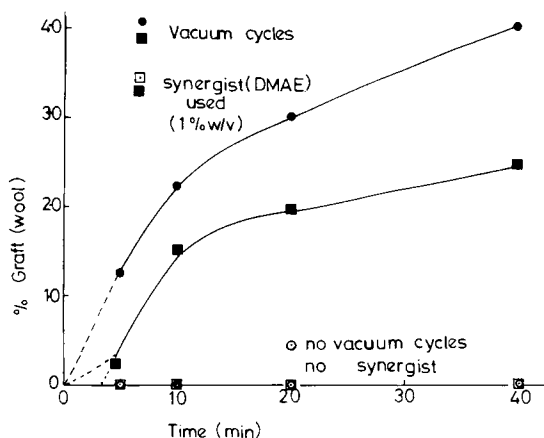
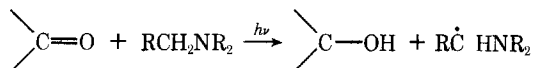


Fig. 3. Variation in % graft (based on wool weight) with time. Vacuum treated wool/medium (●, ■); nonvacuum treated (○, □); synergist (DMAE) applied (□, ■). Monomer concentration 10% (w/v), initiator concentration 0.5% (w/v); grafting at pH = 2.0.

cycles are applied, though the level of grafting is reduced with the synergist DMAE present.

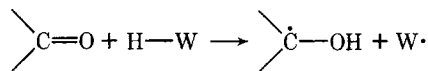
## DISCUSSION

SKS is one of the ketone/amine photoinitiator components. In homopolymerization reactions, it is normally recommended that the "synergist" be included in the formulation. Dimethylaminoethanol is generally accepted as being an efficient "synergist." It is thought that with ketone/amine systems the mechanism of radical initiation is of the type



The radical species,  $\text{R}\dot{\text{C}}\text{HNR}_2$ , is thought incapable of becoming involved in hydrogen abstraction reactions. Hence, it is somewhat difficult to see how SKS/amine combinations can produce graft copolymers. However, other synergist systems are available as proton donors.

Our original approach was to use the substrate as the synergist, thus leaving radical sites on the backbone which would be capable of initiating grafting. For this to apply, the photoinitiator would need to be in close proximity with the substrate. Thus, we have the situation



Here W denotes the proton bearing substrate (in this case, the wool). This being so, one might anticipate that the homopolymerization reaction would be minimized. In fact, in the absence of the synergist, no homopolymerization was detected. With DMAE in the photoinitiating system, homopolymerization was the dominant effect.

Photoinitiated grafting to woolen substrates from aqueous media is facilitated by acidic conditions, though NVP is susceptible to hydrolysis under such conditions. Hence, NVP is not the easiest of monomers to work with in photoinitiated wool grafting. However, under controlled pH conditions one can take advantage of the limited sensitization of the woolen substrate, while keeping hydrolysis of the monomer to a minimum. It is our opinion that grafting is better expressed in terms of the use of the available monomer—to give grafting—rather than in consideration of the increase in weight of substrates. To this end, the padding operation would appear to be a vital feature of efficient use of NVP. A more detailed account of the involvement of the woolen substrate in the photoinitiator process will be given when studies with other monomers are complete.

As yet there is no absolute proof that grafting has taken place in the NVP-wool system under investigation here. Despite great thoroughness in procedures to extract occluded homopolymer, we cannot guarantee that the composites are true graft copolymers. However, it has been shown that SKS is very strongly adsorbed by woolen substrates and that homopolymerization reactions are not efficiently initiated by SKS. Owing to the close proximity of SKS and the wool,

there is every opportunity for radical sites to be generated on the surface of the wool. Hence, grafting becomes a highly feasible possibility. This point is to be examined further.

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