

Deposition of Acrylate Polymers in Wool Fibers

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Synopsis

The factors influencing the kinetics of formation of acrylate polymers in wool fibers are described. Allyl methacrylate and N,N'-methylenebisacrylamide were found to copolymerize satisfactorily with methyl or ethyl acrylate to form crosslinked polymers. Conditions were found for almost complete conversion of the available monomer to polymer in a batch-type process.

INTRODUCTION

In previous papers the kinetics of deposition of polyacrylonitrile in wool were described, the catalyst used being the complex formed between copper acetylacetonate and trichloroacetic acid.¹ This catalyst has proved to be particularly effective in polymerizing polar monomers such as acrylates. Polyacrylates have been applied to wool fiber surfaces to achieve shrinkproofing,² and have been deposited internally by a pre-irradiation technique³ and by ferrous ion-peroxide catalysis.⁴ The results reported here include a study of the kinetics of methyl acrylate polymerization and a brief account of the copolymerization of either methyl or ethyl acrylate with bifunctional monomers. Most attention has been devoted to techniques which might readily be adapted to commercial practice, in particular to efficient batch-type processing.

EXPERIMENTAL

Material

The wool used was mainly scoured 44s-quality Lincoln from which the tip ends were discarded.

Polymerization Methods

Weighed samples of loose wool (0.2 g dry weight) were impregnated in 10 ml of an aqueous solution of copper acetylacetonate and trichloroacetic acid (1.0 g/l. $\text{Cu}(\text{AcAc})_2$ and 2.5 g/l. TCA) brought to pH 3 with ammonia. After impregnation for 10 min at 70°C, the samples were rinsed with distilled water (two changes) for about 1 min, sponged dry, and immersed in the appropriate aqueous solution of monomers and accelerators in a Quick-fit stoppered tube, which was heated in a thermostatted bath for various

polymerization times. The samples were then rinsed in water and dried to determine the weight add-on.

Larger samples (1 kg) were treated in a similar manner in a commercial Vald Henriksen pressure dyer with forced liquor flow through the wool.

Analyses

Nitrogen analyses were performed on a Coleman Analyser. Residual unsaturated bonds in the polymers were estimated by the method of Gallo and co-workers.⁵

RESULTS

Pretreatment of Wool

Considerable differences in the rate of polymerization have been noted when different lots of wool were used. The same effect has been observed in experiments in these laboratories using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ redox initiation methods,⁶ and it appears to be due to the state of the epicuticular layer surrounding the wool fibers, which apparently offers a barrier to permeation of catalyst and possibly monomer. Reasonable consistency between samples was obtained if the wool was first given a mild chlorination (1% Cl on wool weight), and this procedure was adopted throughout.

Effect of Oxygen on Polymerization

Samples were impregnated as described earlier, then immersed after rinsing in 0.2% TCA solutions and evacuated while frozen with liquid nitrogen. Deoxygenated methyl acrylate (MA) was transferred to the sample tube which was then sealed. Other samples were treated with TCA solutions containing either 2% (v/v) of *tetrakis*-hydroxymethyl phosphonium chloride (THPC) or 0.05M Na_2SO_3 as alternatives to the deoxygenation procedure. The polymerization over 30 min at 70°C was compared with that in tubes stoppered without any attempt at deoxygenation and an experiment in which oxygen was passed slowly through the solution during polymerization. The results in Table I indicate that oxygen has an inhibitory effect on polymerization, but that the rudimentary precaution of stoppering the tube is as effective as complete prior deoxygenation. It is also evident that THPC substantially destroys the catalyst.

TABLE I
Effect of Oxygen on Polymerization

Treatment of solution	Add-on, % of polymer ^a
None	72 ± 2
Deoxygenated	74 ± 2
Continuous oxygenation	11 ± 3
2% THPC added	9 ± 1
0.05M Sulfito added	75 ± 2

^a Average of three experiments.

Larger-scale experiments with 1-kg samples in a closed stainless steel container through which monomer solutions were circulated with an external impeller pump were more sensitive to the presence of oxygen in the system. A sulfite concentration of 0.05M eliminated oxygen termination, and polymerization rates comparable to those in the small tubes were attained.

Optimum Catalyst Concentrations

The relationship between concentration of $\text{Cu}(\text{AcAc})_2$ in the impregnation solution and the subsequent deposition of poly(methyl acrylate)

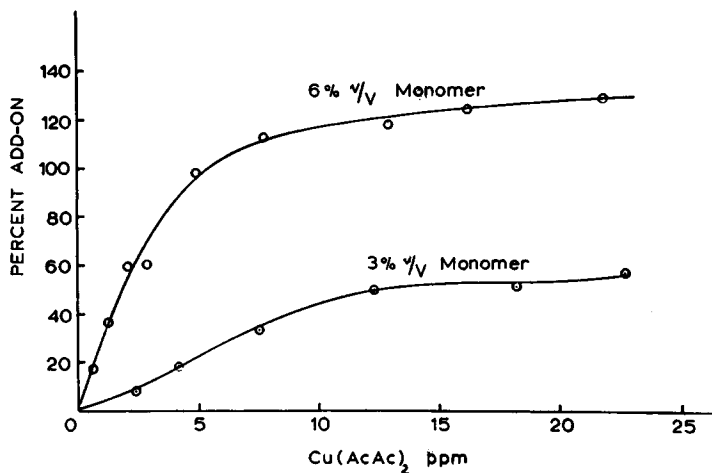


Fig. 1. Dependence of percentage add-on on $\text{Cu}(\text{AcAc})_2$ concentration in impregnation solution. Polymerization time, 35 min at 70°C; MA monomer.

(PMA) was similar to but not identical with that found for polyacrylonitrile⁸ and changed significantly with the initial monomer concentration (Fig. 1). The deposition of PMA increases markedly as the TCA concentration in the polymerization solution is increased from 0 to 3 millimoles/l., i.e., up to $\log(1 + [\text{TCA}]) \approx 0.6$, and more slowly thereafter (Fig. 2). Note that the concentration of TCA shown does not include the very small unmeasured amount which remains in the wool after impregnation and rinsing and accounts for the 6% polymer formed in the absence of additional TCA in the polymerization solution. Solutions of approximately 6 millimoles/l. TCA were unusual in being particularly prone to a sudden and unexplained formation of homopolymer in the solution phase.

Effect of Monomer Concentration, Temperature, and pH on the Rate of Polymerization

Polymerization experiments with monomer concentration $[M]$ as the variable and with low percentage conversions of the available monomer demonstrated that the deposition in a fixed time is proportional to $[M]^2$,

as shown in Figure 3. The typical deposition rate curve in Figure 4 shows that there is a short "inhibition time" and also that the reduction in rate as monomer is consumed is less than that predicted from the $[M]^2$ dependence. High temperatures increase the rate to the same extent as in the polymerization of acrylonitrile, and the pH dependence is also similar.¹

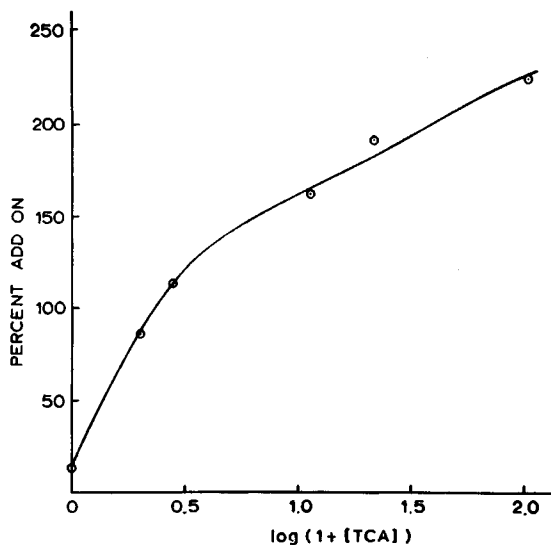


Fig. 2. Dependence of percentage add-on on TCA concentration expressed in millimoles/l. $\text{Cu}(\text{AcAc})_2$ in the impregnation solution, 10 ppm; polymerization time, 35 min at 70°C; 6% (v/v) MA.

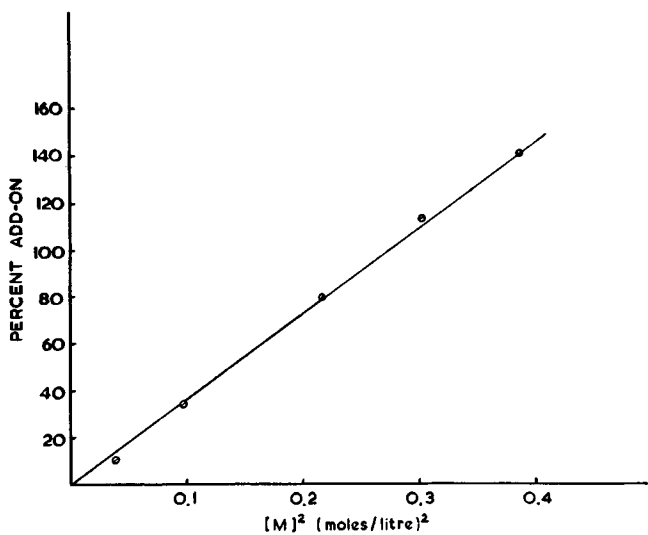


Fig. 3. Dependence of percentage add-on on MA concentration $[M]$. $\text{Cu}(\text{AcAc})_2$ in the impregnation solution, 10 ppm; TCA, 3 millimoles/l.; polymerization time, 35 min at 70°C.

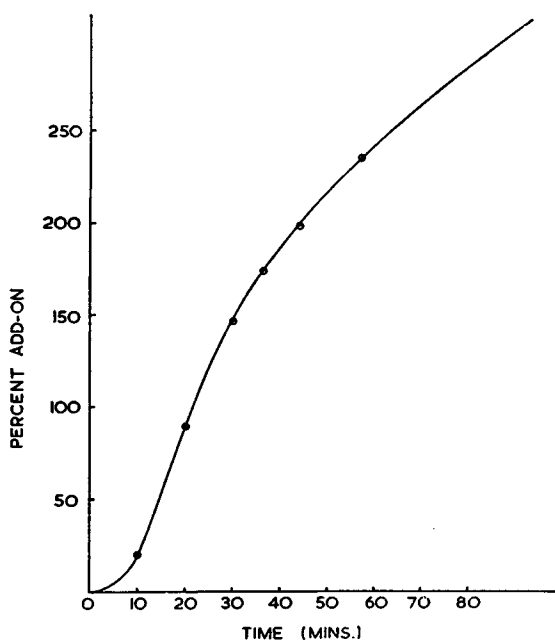


Fig. 4. Polymerization rate at 6% (v/v) MA. Other conditions as in Figure 3.

Pressure Dyer Experiments

Under the conditions of forced liquor flow in this equipment, the effect of dissolved oxygen was more noticeable, and 0.05M Na_2SO_3 was used as an oxygen scavenger. Monomer conversions of 95–100% were obtained after 1½ hr polymerization at 70°C with 0.2% TCA, 10:1 liquor:wool ratio, and polymer add-ons of the order of 70–80%.

It was also found possible to simplify the processing procedure to a “one bath” system in which 0.08% $\text{Cu}(\text{AcAc})_2$ on wool weight was circulated with TCA, monomer, and sulfite as the temperature was raised, i.e., the separate impregnation and rinsing cycles were eliminated. The proportion of unbound polymer formed was usually small and could be reduced still further by delaying the introduction of the sulfite for about 10 min.

Polymerization of Ethyl Acrylate and Crosslinked Acrylates

Ethyl acrylate (EA) polymerizes in wool in a similar manner to MA, but in exhaustion experiments the efficiency of conversion is usually 85–95% rather than 90–100%. Two bifunctional monomers were found which copolymerized with either MA or EA to form insoluble crosslinked polymers. Copolymers of N,N'-methylenebisacrylamide (MBA) and MA formed in solutions at low percentage conversion were analyzed for nitrogen content. The mole ratios determined permitted approximate values of the relative monomer reactivity ratios to be calculated from a Fineman-Ross plot. The ratio of the rate constants for the reaction of MA radical with MA

as compared to MBA was 0.35, and the corresponding ratio for MBA radicals was 1.6.

Nitrogen analyses of wool containing MA-MBA copolymers indicated a higher proportion of MBA than in solution polymerization in spite of the fact that MBA is a much bulkier monomer, with presumably a lower diffusion rate. The discrepancy tends to disappear at copolymer add-ons greater than 50%. Solutions of high MBA concentration were prone to produce homopolymer in solution, but at MA:MBA ratios between 5:1 and 10:1, nearly complete conversion of total monomers to copolymer inside the wool was achieved.

Allyl methacrylate (AMA) also copolymerizes rapidly and efficiently (>90%) with MA and EA and is not so prone to form polymers in the solution phase. Polymerization rates do not vary greatly with different AMA concentrations, implying that the monomer reactivity ratios are closer to unity than in the case of MBA copolymerization.

Verification of Crosslinking in Copolymers

Copolymers containing a proportion of MBA were analyzed for residual unsaturated bonds.² It was found that the reaction between iodine and the unsaturated bonds of MBA was slower than for isoprene-isobutylene copolymers⁷ but had the same stoichiometry, i.e., three atoms of iodine for each unsaturated bond. Taking monofunctional polymerization as 100% unsaturation and complete bifunctional polymerization at 0%, it was found that MBA incorporated in MA copolymers in solution or in wool was 14% unsaturated, indicating a high level of crosslinkage formation.

CONCLUSIONS

The mechanism of initiation of polymerization in aqueous systems with $\text{Cu}(\text{AcAc})_2$ -TCA is uncertain. The rate of AN polymerization in wool was found to be proportional to AN concentration in solutions of AN in water, but a different mechanism is probable in AN saturated with water.¹ Acrylates have been shown in this work to polymerize by yet another mechanism with a rate dependent on $[\text{M}]^2$. The latter result suggests that these polar monomers interact with the $\text{Cu}(\text{AcAc})_2$ -TCA complex to initiate polymerization. Examples of this behavior have been reported recently.⁷ The pH dependence of the polymerization rate probably reflects changes in the decomposition mechanism of the catalyst complex. It may be significant that the optimum pH is at the upper end of the titration range of trichloroacetate ion ($\text{pK} \approx 2$) even though the stability of the $\text{Cu}(\text{AcAc})_2$ -TCA complex apparently decreases with increasing pH (unpublished spectroscopic data).

The polymerization conditions for efficient conversion of available monomers appear to be suitable for industrial processing and have some obvious advantages over others devised for deposition inside wool fibers. A "single bath" procedure proved feasible because the small amount of

$\text{Cu}(\text{AcAc})_2$ available was rapidly absorbed by the wool so that homopolymer formation was negligible. At the conclusion of polymerization, the solution is at pH 5-6, and no neutralization is necessary (cf. $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and persulfate initiation). Sulfite is an effective and cheap oxygen scavenger, and when used under the present conditions it has a negligible degradative effect on the wool substrate. In contrast, reactions between THPC and persulfate with wool cystine^{8,9} are possible side effects of their use in polymerizations in wool.

The acrylate copolymers particularly suitable for $\text{Cu}(\text{AcAc})_2$ -TCA initiation afford a range of hard (MA-MBA copolymers) to soft (MA or EA polymer) additives with which to modify the properties of wool.

Work in progress indicates that it is also possible to vary the site of deposition of polyacrylates in wool, and the effects of doing this on textile and other properties will be reported later.

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