

Graft Copolymerization of Acrylic Acid to Nylon 6 by Mutual Irradiation. II. The Influence of Cupric Ions

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Synopsis

In the γ -irradiation in vacuo of nylon 6 film in the presence of aqueous acrylic acid and different concentrations of cupric chloride, the following relationships have been obtained: $R_H \propto [\text{CuCl}_2]^{-1.0}$ and $R_G \propto [\text{CuCl}_2]^{-0.3}$. Here $[\text{CuCl}_2]$ is the concentration of cupric chloride in the bulk solution, and R_H and R_G denote the initial rates of homopolymerization and grafting, respectively. The values of -1.0 and -0.3 for the exponents indicate that the cupric ion is a less effective chain terminator in the film on account of its lower concentration there. Analyses of films grafted in different media demonstrate the copper content of a film to be independent of both the concentration of monomer in the solution and the degree of swelling. The copper content is primarily a function of the total poly(acrylic acid) present, i.e., grafted species plus occluded homopolymer). Thus, at high doses, where the total poly(acrylic acid) associated with a film is significant, the grafting curves exhibit a falling off, and complex formation between cupric ion and a growing chain is considered a likely contributory factor.

INTRODUCTION

The γ -irradiation-initiated grafting of acrylic acid to nylon 6 exhibits a marked tendency toward homopolymerization, and, in extreme cases, any quantitative estimation of the extents of grafting and homopolymerization is rendered almost impossible because of the formation of a crosslinked gel. In a short preliminary communication (to be regarded as Part I of this series),¹ it was noted that, at a fixed dose, certain transition metal cations could be used to suppress the homopolymerization and grafting processes. Of the ions investigated, Cu^{2+} was the most effective.

The purpose of the present work is to elucidate the exact dependences of the initial rates of grafting (R_G) and homopolymerization (R_H) on the concentration of added cation. Consequently, full kinetic curves of the two processes as a function of dose have been obtained for each $[\text{Cu}^{2+}]$ (in the form of cupric chloride). Furthermore, although the concentration of cupric ion in homogeneous homopolymerization may reasonably be identified with its initial value in the bulk solution, it should be noted that the grafting on to nylon 6 film proceeds in a swollen medium. Hence it has

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also been considered necessary to determine the concentration of copper in the grafted film for several degrees of swelling (by the aqueous monomer) and over a range of degrees of grafting in each of the monomer-solvent media.

EXPERIMENTAL

As in the previous work,¹ radiation was effected by γ -rays from a 9000-Curie ^{60}Co source and the dose rate determined by Fricke dosimetry. Nylon 6 film of thickness $80\ \mu$ was used throughout.

Glass ampoules containing the film and a solution comprising 10 vol-% aqueous acrylic acid and cupric chloride at the desired concentration were outgassed by freeze-thaw cycles, sealed (10^{-5} mm), and irradiated at $30^\circ \pm 0.1^\circ\text{C}$ at a dose rate of 18.4 rad/min. After irradiation the extracted film was washed repeatedly with hot water and then methanol, and dried to constant weight in vacuo at 40°C . The degree of grafting was estimated directly from the increase in weight.

For the rate experiments at several values of $[\text{CuCl}_2]$, approximately 0.1 g of film in 10 ml monomer solution was employed. When neutron activation analysis for the concentration of copper in film was to be carried out, two films in a correspondingly larger volume of monomer solution were used in each ampoule. After irradiation, the two films were subjected to different treatments, viz., for the first film the normal extraction of homopolymer and drying to constant weight were carried out in order to find the degree of grafting. The second film was surface dried between filter papers and then completely dried to constant weight in vacuo. The resultant increase in weight of this second film represents those weights due to both grafted poly(acrylic acid) and ungrafted homopolymer formed within the film during the grafting process. The copper contents of the nonextracted (i.e., the second) films were determined by neutron activation analysis at the Universities Research Reactor, Risley, Lancashire, England, and were quoted in units of ppm (parts per million) by weight.

Homopolymerization in the bulk solution was estimated immediately after irradiation by the following method: Dilute aqueous NaOH was added in slight excess to the solution, the homopolymer and unreacted monomer thus being converted to their sodium salts and the metal ion (Cu^{2+}) to its insoluble hydroxide. After addition of the resultant mixture to a large excess of methanol, the poly(sodium acrylate) precipitated and the cupric hydroxide still remained insoluble. The cupric hydroxide and poly(sodium acrylate) were filtered, washed, and weighed, and the degree of homopolymerization was calculated as a percentage conversion by weight, making due allowance from a blank experiment for the inorganic material present. This procedure is essentially the same as the one used previously,¹ except that cupric ions were not removed prior to precipitation of the poly(sodium acrylate) with methanol.

RESULTS

The Copper Content of Grafted Films

Nylon 6 films containing both grafted poly(acrylic acid) and homopolymer were prepared in five different media, viz., 5, 10, 20, 30, and 40 vol-% aqueous acrylic acid. In each case the overall concentration of cupric chloride was $10^{-3} M$. As indicated in the experimental section, the dried films were subjected to neutron activation analysis to obtain the copper content. The results are shown in Figure 1, which demonstrates that, as the total poly(acrylic acid) content of the films increases, there is an accompanying rapid rise in their copper content. Furthermore, all the points

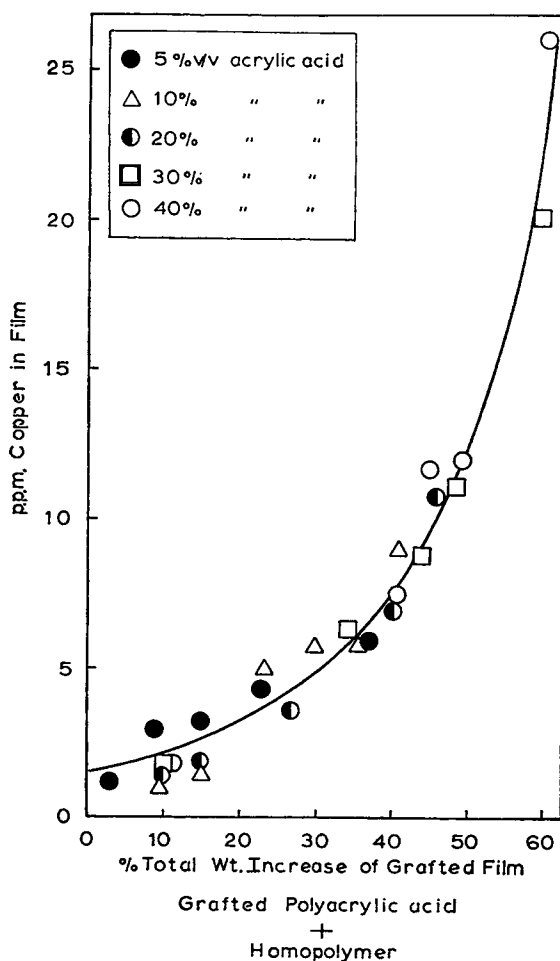


Fig. 1. Copper content of films vs. total weight increase of films grafted in different media. As indicated, the total weight increase is composed of grafted poly(acrylic acid) and ungrafted homopolymer.

lie approximately on the same curve regardless of the nature of the grafting medium, i.e., [acrylic acid]. As the degree of swelling is dependent on [acrylic acid], the same curve fits all the points regardless of the degree of swelling. These observations indicate that the copper content of the film is primarily a function of the poly(acrylic acid) content and is not directly dependent on its degree of swelling. This conclusion is substantiated by copper analyses that had been performed on ungrafted films swollen in the

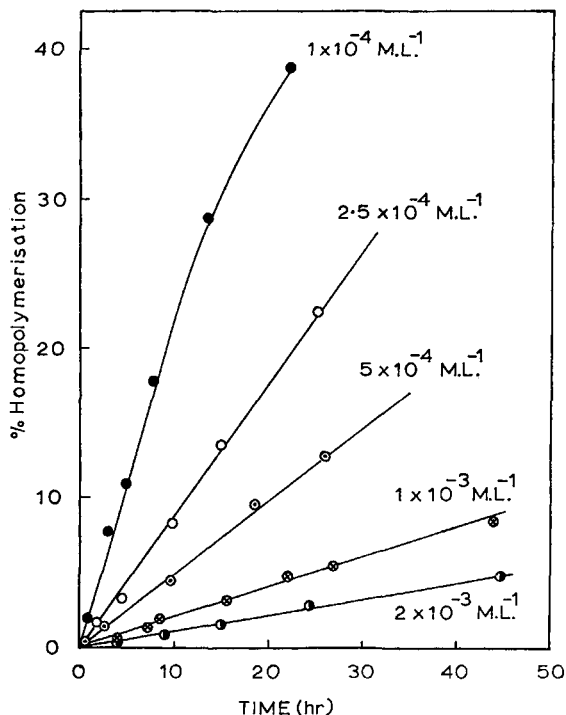


Fig. 2. Rate plots for the γ -irradiation-initiated homopolymerization of acrylic acid in aqueous solution in the presence of CuCl_2 at the molar concentrations indicated. Initial monomer concentration is 10 vol-% in each case.

various reaction media. In this range of [acrylic acid], a high initial swelling of 19.9 to 55.7 wt-% was observed, whereas the copper contents of these poly(acrylic acid)-free films lay in the very narrow range of 1.3 to 1.9 ppm and may be regarded as small and constant in comparison with the copper contents obtained for grafted films (cf. Fig. 1).

As the monomer concentration in the grafting medium is increased, there is a widening discrepancy between the degree of grafting (obtained from the first films) and the total gain in weight (obtained from the second films), which comprises both grafted poly(acrylic acid) and unremoved poly(acrylic acid) homopolymer. This indicates that homopolymerization occurs within the film to an extent which becomes more significant at high concentrations of monomer in the medium.

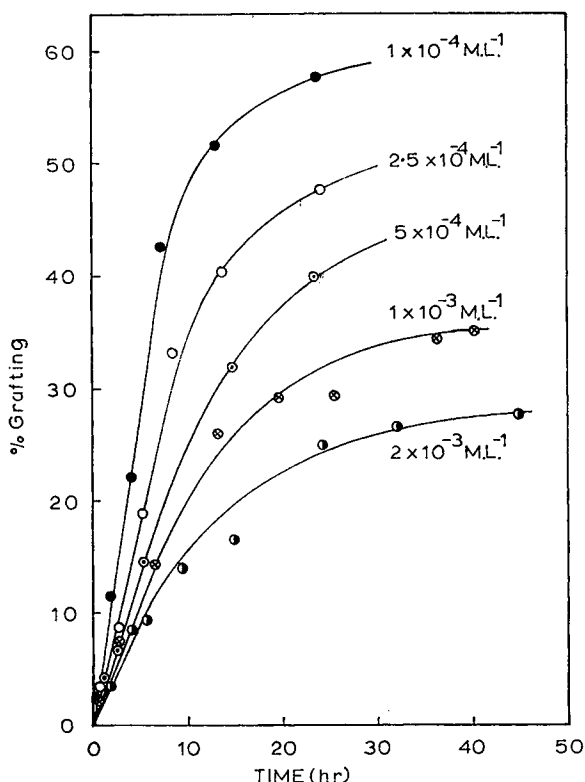


Fig. 3. Rate plots for the γ -irradiation-initiated grafting of acrylic acid to nylon 6 in the presence of CuCl_2 in the bulk solution at the molar concentrations indicated. Initial monomer concentration in the bulk solution is 10 vol-% in each case.

Effect of $[\text{CuCl}_2]$ on Rates of Grafting and Homopolymerization

The concentration of monomer was 10 vol-% in all cases, and that of CuCl_2 in the bulk solution was varied from 1×10^{-4} to 2×10^{-3} mole/l. Each experiment yielded rate curves for both homopolymerization and grafting, and the plots are given in Figures 2 and 3, respectively, at each $[\text{CuCl}_2]$. In Figure 2, the homopolymerization is seen to increase linearly with time, or total dose, except for the highest two times on the curve for the lowest $[\text{CuCl}_2]$, and it is clear that there is a serious depletion of monomer in this region. In contrast, the grafting curves in Figure 3 all display a tailing off at high dose after an initially linear region. Induction periods of 0 to 2.4 hr were observed in both reactions as a result of residual traces of air in the system (probably within the film rather than the bulk solution) after out-gassing. These have been corrected for in Figures 2 and 3 by displacing the time axes so that the plots proceed from the origin.

The dependences of the initial rates of homopolymerization and grafting on the concentration of cupric chloride are represented by log-log plots in Figures 4 and 5, respectively. The slopes of these yield

$$R_H \propto [\text{CuCl}_2]^{-1.0}$$

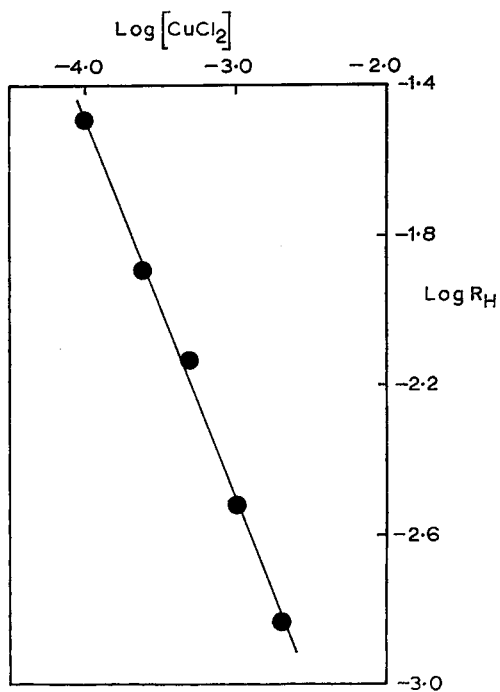


Fig. 4. Dependence of initial rate of homopolymerization on the concentration of added CuCl_2 .

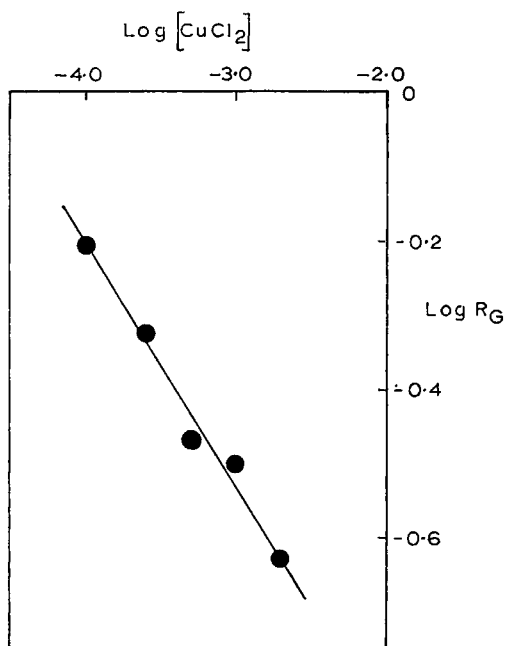


Fig. 5. Dependence of initial rate of grafting on the concentration of CuCl_2 in the bulk solution.

and

$$R_G \propto [\text{CuCl}_2]^{-0.3}.$$

In plotting Figures 4 and 5, the values of R_H have been converted from wt-% per hour (from Fig. 2) to mole/l. per hour, and those of R_G from wt-% per hour (from Fig. 3) to mole/l. of swollen film per hour.

DISCUSSION

In both grafting and homopolymerization, the influence of the added salt is in the same direction, i.e., as $[\text{CuCl}_2]$ in the bulk solution is increased, the rates of these processes fall. This decrease has been demonstrated¹ to result from the electron transfer reaction between a growing poly(acrylic acid) radical and the cupric ion or some complex of it. The exponents of -0.3 and -1.0 obtained for the dependences of R_G and R_H , respectively, on $[\text{CuCl}_2]$ indicate that the cupric ion is a less effective chain terminator in the film than in the bulk solution, probably because of its lower concentration. (Note that the values of $[\text{CuCl}_2]$ refer to those in the bulk solution.) For example, in the case of $[\text{CuCl}_2] = 1 \times 10^{-3}$ mole/l. ($\equiv 60$ ppm) in the bulk solution, the copper content of the film throughout grafting ranges only from 0.9 to 9.0 ppm. Despite the low concentration of copper in the film relative to that outside, there is nonetheless an increase in the copper content of the film during grafting, and this is considered to contribute to the tailing off found in the later stages of reaction (Fig. 3). The reasons why the grafting curves under these and other conditions have the observed shape have been investigated fully and will be discussed in a later paper of this series.

Cupric ions are known to complex with poly(acrylic acid) in aqueous solution, and such complex formation is clearly feasible during the two types of polymerization occurring here. Some doubt exists as to whether the coordination number is two² or four³; but, even taking the lower number, the concentration of poly(acrylic acid) in the film is always a factor of at least 10^4 in excess of that required to completely complex all the copper present. However, the possibility that the copper may be complexed in some way with the poly(acrylic acid) is a real one and raises the question of whether the termination mechanism is dominated by the complex as opposed to the aquated cupric ion.

Bengough and co-workers⁴⁻⁶ have studied the role of cupric chloride in the polymerization of several vinyl monomers and concluded that the reaction between metal ion and polymer radical is controlled by factors other than the reactivity of the polymer radical, as measured by copolymerization studies. They suggested the possible involvement of different types of chloro complex. However, these workers utilized a nonaqueous solvent (dimethylformamide), which would promote chloro complex formation more readily than the dilute aqueous solutions used in the present work.

A more direct comparison with our experiments is afforded by the results of a systematic study by Dainton and co-workers^{7,8} of the effects of several metal ions on the polymerization of acrylamide in dilute aqueous solution. It was recognized that water molecules of the inner or outer hydration spheres of the metal (M^{z+}) or hydrolyzed, oxygenated, or even polymeric forms of M^{z+} might be involved in the rate-determining step. All attempts to correlate the rate constants or the activation energies with properties of the redox system, such as ionization potential, were unsuccessful, and the authors concluded that entirely nonthermodynamic factors dominate these reactions.

However, it was observed that metal ions with incomplete *d*- or *f*-shells (Cu^{2+} and Fe^{2+}) react rapidly with a growing polymer radical, whereas those with complete *d*-shells either react very slowly (Hg^{2+} and Ti^{3+}) or not at all (Ag^+). In the present investigation, the relevant ions are Cu^{2+} and, as reported previously, Fe^{2+} and Fe^{3+} . All these possess available *d*-orbitals, which may be utilized for the proposed electron transfer in homopolymerization and grafting.

It should be stressed that these comparisons merely afford some measure of qualitative support for the proposed role of the ions. Neither Dainton et al.^{7,8} nor the present authors provide a definitive explanation which can be generalized to include all cases. In this connection it is particularly pertinent to note that in the grafting of acrylic acid in aqueous solution to preirradiated poly(ethylene terephthalate), Robalewski and Stolarczyk⁹ observed LiI, NaI, and KI to selectively suppress homopolymerization, with a definite but smaller effect on the grafting.

The effect of varying the anion and the temperature has a direct bearing on the role of cupric ions. These and other aspects of the system will be reported in later papers of this series.

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References

1. M. B. Huglin and B. L. Johnson, *J. Polym. Sci. A-1*, **7**, 1379 (1969).
2. F. T. Wall and S. J. Gill, *J. Phys. Chem.*, **58**, 1128 (1954).
3. H. Morawetz, *J. Polym. Sci.*, **17**, 442 (1955).
4. W. I. Bengough and T. O'Neill, *Trans. Faraday Soc.*, **64**, 1014 (1968).
5. W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc.*, **64**, 382 (1967).
6. W. I. Bengough and W. H. Fairservice, *Trans. Faraday Soc.*, **61**, 1206 (1965).
7. E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel and (in part) S. Tazuké, *Disc. Faraday Soc.*, **29**, 188 (1960).
8. F. S. Dainton and M. Tordoff, *Trans. Faraday Soc.*, **53**, 499 (1957).
9. A. M. Robalewski and L. W. Stolarczyk, *Nukleonika*, **15**, 55 (1970).

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