The Xanthate Method of Grafting.   II.   Effect of Operating Conditions on the Grafting of Acrylonitrile onto Wood Pulp

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Synopsis

Wood pulp was copolymerized with acrylonitrile as a monomer using the xanthate grafting method. This method takes advantage of the capability of cellulose xanthates to form a redox couple with a suitable oxidation agent. The present work uses the degree of xanthation $\gamma \doteq 5$ and hydrogen peroxide as an oxidant. Experiments carried out under different conditions have permitted to evaluate the influence of various reaction parameters on the graft copolymerization. Among the factors investigated, two appeared to be of a paramount importance: the initial pH of the reaction mixture and the concentration of hydrogen peroxide. A change in one of these parameters produced profound effects on the total conversion to polymer as well as on the copolymer:-homopolymer ratio. By a suitable combination of initial pH and peroxide concentration, it was possible to synthesize graft copolymers whose homopolymer content approaches zero.

INTRODUCTION

Among the various methods suggested for the grafting of vinyl monomers onto cellulosic and lignocellulosic substrates, the xanthate method[1] appears to have a number of distinct advantages. Firstly, the process can utilize viscose, an industrial intermediate, as the primary material. Secondly, unlike in many other methods, the formation of initiating species can be carried out directly on the backbone chain; this is linked directly to the parameter of grafting efficiency in that the formation of homopolymer is minimized. Finally, the process does not require an inert atmosphere and other special conditions nor does it necessitate the use of expensive reagents. It is not surprising, therefore, that the xanthate method has already found some practical applications.[2,3]

Various aspects of the xanthate process have already been tackled by different researchers. Notably, Dimov and Pavlov[4] have studied the effect of changing the conditions of the reaction, using bleached cotton calico as grafting substrate and acrylonitrile as monomer. Their results indicated low homopolymer contents of the products obtained, especially when using substrates with high xanthate content.

Kokta and Valade[5] have studied, on the other hand, the effect of using binary mixtures of monomers. They have found that small quantities of monomers such as acrylonitrile or acrylamide promoted the grafting of styrene onto bleached pulp. Such synergetic effects, which have been detected earlier with a number of comonomer pairs,[6,7,8] can greatly improve the efficiency of some graft copolymerization systems.

The present study was undertaken with the aim to evaluate, in a manner as comprehensive as possible, the influence of changing various reaction parameters on the grafting reaction. Acrylonitrile was selected as the monomer in order that a comparison could be made with other studies previously published by different authors, which mostly use the same monomer. Kraft semibleached pulp has been used throughout as the grafting substrate.

EXPERIMENTAL

Copolymerization

The technique of pulp preconditioning as well as the copolymerization procedure have been described in a previous paper.[5] Unless specified otherwise in each separate case, the experimental conditions used were as follows: pulp, approx. 4.5 g $\pm$ 0.01 g (oven-dry weight); monomer (acrylonitrile), 9.09 g; surfactant, Tween-40; 0.9 g; H_2O_2, 1.5 g (diluted into 25 ml before adding); mercerization, 45 min in 150 ml 0.75 N NaOH (room temperature); xanthation, 2 hr (room temperature); ion exchange, 2 min in 150 ml 0.004% solution of $(NH_4)_2Fe(SO_4)_2$; initial pH, 5 $\pm$ 0.1 (adjusted with 0.1 N H_2SO_4); reaction temperature, 25°C.

The degree of xanthation of the pulp obtained by using this procedure was determined by a modified iodometric titration method. It was found to be $\gamma = 5 \pm 0.4$ (i.e., approx. 5 xanthate groups per 100 units of glucose).

The pulp used in all the experiments discussed in this article (Kraft semibleached; lignin content = 0.8%; viscosity (CED) = 12.7 cps) was supplied by Consolidated Bathurst and was used as such without further chemical treatment. Acrylonitrile was purified by distillation and preserved in the refrigerator. All the other reagents and materials were used such as supplied by the manufacturers.

The quantity of homopolymer in the reaction products was determined by a Soxhlet extration of 2–3 g samples with dimethylformamide. The extractions were carried out under vacuum (20–30 mm Hg) in order to minimize degradation processes. The calculations concerning the grafting parameters (total conversion, polymer loading, and grafting efficiency) have been made taking into account the loss of pulp during mercerization due to its solubility in NaOH (about 3.5%).

The grafting parameters are defined as follows:

$$\text{Total conversion, } \% = (D\text{-}B)/C \times 100$$
$$\text{Polymer loading, } \% = (A\text{-}B)/B \times 100$$
$$\text{Grafting efficiency, } \% = (A\text{-}B)/(D\text{-}B) \times 100$$

where A is weight of products after copolymerization and extraction, B is weight of pulp (oven dry, corrected for solubility in NaOH solution), C is weight of monomer charged, and D is weight of products after copolymerization.

Molecular Weights

All molecular weights reported in this article have been determined by viscometry. For the molecular weight of copolymers, the extracted products were treated with a mixture of acetic acid, acetanhydride, and sulfuric acid according to the procedure described by Rogovin and co-workers[9] and the residue extracted with warm dimethylformamide. For homopolymers, a sample of unextracted products was shaken with warm dimethylformamide; the residue was subsequently filtered off and the filtrate collected.

In both cases, viscosity was recorded at 30°C in dimethylformamide at four different concentrations in Ubbelohde viscometers. Following extrapolation to obtain the intrinsic viscosity $[\eta]$, the corresponding molecular weights were calculated according to the expression[9]

$$[\eta] = 0.392 \times 10^{-3} M^{0.75}.$$

RESULTS AND DISCUSSION

Before discussing the experimental results, two important points should be mentioned. Firstly, in order to make possible a quantitative evaluation of the copolymer:homopolymer ratio with a reasonable accuracy, it is necessary to work with products having a sufficiently high polymer add-on. To satisfy this requirement, a rather high monomer:pulp ratio has been used in these experiments (2:1). Secondly, the presence of significant quantities of homopolymer must be ensured in order that its removal by extraction bring about a detectable loss of weight. Consequently, the experiments listed below often forsake the ideal reaction conditions (those restricting the formation of homopolymer) in favor of conditions under which grafting efficiency of approximately 50–60% is achieved. This is mainly accomplished by using a low concentration of hydrogen peroxide in the system.

As well as in other redox systems, the reaction of partial cellulose xanthates with hydrogen peroxide (and consequently the rate of formation of initiating radicals) shows a marked dependence on the pH of the reaction mixture. [The term "partial cellulose xanthates" stands for xanthates bound statistically to any component of the pulp (cellulose, hemicellulose, lignin).] Dimov and Pavlov[4] have demonstrated that in their system, grafting occurred mainly at a very low pH (1–2), while pH 3 gave rise to the lowest polymer add-on. Further increase in pH then brought about a slow rise in polymer add-on.

The present system behaves quite differently, as is evident from Table I and Figure 1. One observes that, while the total conversion to polymer is still the highest at low pH ~1, the corresponding grafting efficiency is

TABLE I
Effect of Initial pH on Grafting[a]

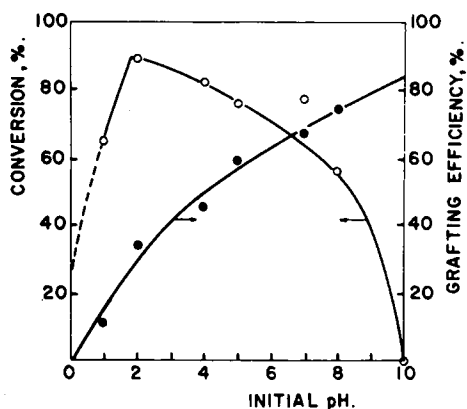| Sample	pH Initial	pH Final	Total conversion, %	Polymer loading, %	Grafting efficiency, %
64	1.0	1.1	64.8	15.1	11.1
44	2.0	2.0	89.2	63.7	34.1
42	4.0	3.3	82.5	79.1	45.8
60	5.0	3.1	76.0	92.3	59.1
59	7.0	3.1	77.4	109.5	67.3
63	8.0	3.0	56.3	88.2	74.7
65	10.0	7.1	0.2	0.4	100.0

[a] 18 Hours of reaction time.

Fig. 1. Dependence of grafting on initial pH.

surprisingly low. The maximum total conversion is observed at pH = 2; it decreases thereafter until it reaches zero conversion at pH = 10. The grafting efficiency, on the other hand, increases rapidly during the same interval from 11.1% at pH 1 to 74.7% at pH 8. It is possible to conclude that the ideal pH at which the reaction may be carried out with an optimum conversion–efficiency relationship would be in the proximity of the intercept of the two curves, viz., pH 5–7.

The grafting efficiency corresponding to this optimum pH is about 60–70%, and the products thus contain rather large amounts of homopolymer. Experiments were carried out to find out if a change in one of the reaction conditions could raise the grafting efficiency. Such a factor has been found in the concentration of hydrogen peroxide, and the appertaining results are summarized in Table II. It is evident that, in the interval studied, the grafting efficiency increases substantially with the amount of H_2O_2 added. The formation of homopolymer is almost prohibited when 9 g H_2O_2 is added.

Of a particular interest is the dependence of polymer molecular weight on the concentration of hydrogen peroxide (Fig. 2). In order that a

TABLE II
Dependence of Grafting on H_2O_2 Concentration[a]

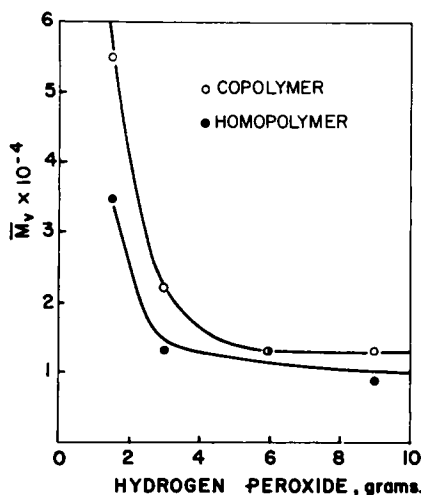| Sample	H_2O_2, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Molecular weight	
					Homopolymer	Copolymer
49	1.50	39.9	51.9	61.6	35,000	55,000
92	3.00	38.6	61.6	76.2	13,000	22,000
93	6.00	47.9	83.2	83.0	13,000	13,000
94	9.00	55.6	107.3	92.5	9,000	13,000

[a] 1 Hour of reaction time.

Fig. 2. Dependence of polymer molecular weight on the concentration of hydrogen peroxide.

substrate material be effectively modified by the grafted polymer, it is mandatory that the latter consist of short chains uniformly distributed along the backbone. The grafted copolymer (i.e., the polyacrylonitrile chains bound to the substrate) in the present system has a molecular weight of about 50,000 at the lowest concentration of H_2O_2. This value decreases rapidly as the peroxide concentration increases, and this drop seems to level off when more than 6 g H_2O_2 is added.

Figure 2 shows also the molecular weights of homopolymers obtained in the same experiments. They appear to be somewhat lower than their copolymer counterparts, but they also decrease with H_2O_2 concentration in the interval covered by these experiments.

On the basis of the foregoing discussion, it would thus appear that the favorable effect of increasing H_2O_2 concentration is twofold: firstly, it almost eliminates the formation of homopolymer, and secondly, it leads to the formation of a greater number of grafted chains and thereby to a more effective modification.

TABLE III
Copolymerization Experiments with Buffers[a]

Sample	Buffer	Concn. of Buffer, mole/l.	pH Initial	pH Final	Total conversion, %	Polymer loading, %	Grafting efficiency, %
45	Potassium hydrogen phthalate	0.5	4.0	4.0	38.5	13.4	17.4
46	Potassium hydrogen phthalate	0.05	4.0	4.0	73.0	75.4	51.5
47	Potassium hydrogen phthalate	0.005	4.0	3.0	62.2	46.9	37.7
31	Secondary sodium citrate	0.1	5.0	5.0	23.0	24.2	46.6
32	Secondary sodium citrate	0.01	5.7	5.0	19.6	17.2	44.2
7	Sodium acetate and acetate acid	0.141 0.059	5.0	5.0	23.2	23.6	47.8
9	Sodium acetate and acetic acid	0.032 0.012	5.5	5.2	38.8	34.0	41.3
90	Secondary sodium phosphate	0.024	9.0	6.9	4.1	0.7	8.1
91	Secondary sodium phosphate	0.010	9.0	6.0	13.4	6.0	21.3

[a] 18 Hours of reaction time.

The molecular weights shown here compare well with results reported by other authors. Faessinger and Conte[1] obtained molecular weights of 10,000–50,000 with various monomers using the xanthate process. In other systems, for example, Arthur and co-workers have found molecular weights of 1,000,000 and 9,000 for copolymers prepared by the postirradiation grafting technique and by the ceric ion-initiated process, respectively. Su and Goldstein[11] have observed rather low molecular weights ($2–15 \times 10^3$) in their system using the Fe^{2+}–H_2O_2 initiating redox system.

It should be noted that the pH values plotted in Figure 1 represent the initial pH. If the pH of the reaction mixture is adjusted initially to a value higher than pH 3, it begins to drop as soon as H_2O_2 is added, and this decrease continues until a constant pH of approx. 3 is reached. This pH drop is complete in some 45–60 min, and a greater part of the copolymerization thus takes place at a pH other than the initial one. Taking this into account, an attempt was made to obtain more reliable (and better defined) results with systems wherein the pH was kept constant by the addition of buffers. The results obtained with various buffer systems are compiled in Table III. It is remarkable that in all but one case the resulting total conversion was markedly inferior to that observed in the absence of buffers. The corresponding values of grafting efficiency show even more clearly that the presence of buffers exerts a deleterious

TABLE IV
Dependence of Grafting on Reaction Time

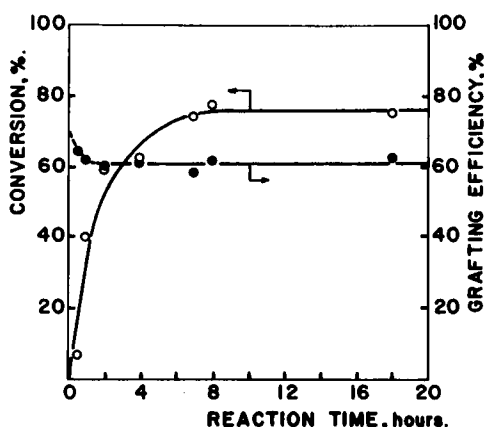| Sample	Time, hr	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Molecular weight	
					Homopolymer	Copolymer
48	0.5	6.7	8.6	64.5	—	46,000
49	1	39.9	51.9	61.6	35,000	55,000
50	2	58.8	72.2	59.9	61,000	33,000
51	4	62.3	77.6	60.9	58,000	26,000
52	7	74.2	88.4	58.2	58,000	24,000
53	8	77.7	96.7	61.8	41,000	22,000
57	18	75.0	98.3	62.6	38,000	18,000

Fig. 3. Dependence of total conversion and grafting efficiency on reaction time.

effect on the copolymerization reaction and that this effect is in turn proportional to the concentration of the buffer. Relatively the best results have been found when using the phthalate buffer; the grafting efficiency is nevertheless unsatisfactory. On the basis of these findings, all the experiments discussed further in the text have been made with systems involving no buffers and which were initially adjusted to pH 5 by an addition of diluted sulfuric acid.

The results presented in Table IV reflect the dependence of grafting on reaction time. The total conversion and the grafting efficiency are plotted against time in Figure 3. It is seen that a rapid polymerization takes place during the first 2 hr of the reaction; the rate then decreases, and after about 8 hr of reaction the system is no longer active. It is interesting to note that, with an exception of the two starting points (30 and 60 min of reaction), grafting efficiency does not vary in the interval covered by these experiments. The slightly higher grafting efficiency at the start of the reaction might be due to the higher pH of the reaction mixture during that stage of the reaction.
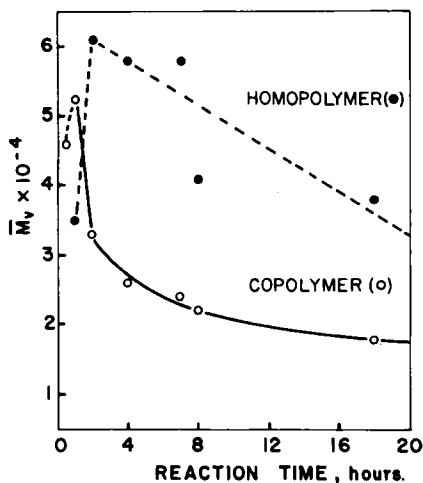
Fig. 4. Copolymer and homopolymer molecular weight as a function of reaction time.

Figure 4 shows the molecular weight results pertaining to the experiments discussed in the foregoing paragraph. It is evident that the molecular weight of the copolymerized polyacrylonitrile decreases as a function of the reaction time. Molecular weights of the homopolymer seem to follow a similar pattern, but their absolute values are higher than those corresponding to the copolymers. In both cases, and especially in the case of the homopolymers, a relatively lower molecular weight is observed in the initial phases of the reaction. After reaching a maximum (at 30–60 min), the molecular weight drops rather rapidly.

The difference found between homopolymer and copolymer molecular weights can perhaps be explained on the basis of a different environment surrounding the two growing chains. Homopolymerization of acrylonitrile is by its nature heterogeneous; unlike its water-soluble monomer, polyacrylonitrile is insoluble in the aqueous phase. This type of a system is known to produce high molecular weight polymers. On the other hand, the loci of formation of the grafted copolymer are inevitably found in the vicinity of cellulose (or other pulp components). This most likely brings about chain transfer reactions caused by —OH groups or by another chain transfer agent. For example, these experiments use a Kraft pulp which has not been completely delignified; the remaining lignin contains —SH groups having pronounced transfer and/or retarding properties.

The next set of experiments has been done to establish the effect of monomer concentration on grafting. The results obtained are summarized in Table V. Figure 5 shows the dependence of total conversion and grafting efficiency on the quantity of monomer used. It appears that while the total conversion increases with growing monomer concentration, the grafting efficiency decreases at the same time. This indicates the homopolymerization reaction is favored by the presence of more monomer.

TABLE V
Effect of Monomer Concentration on Grafting[a]

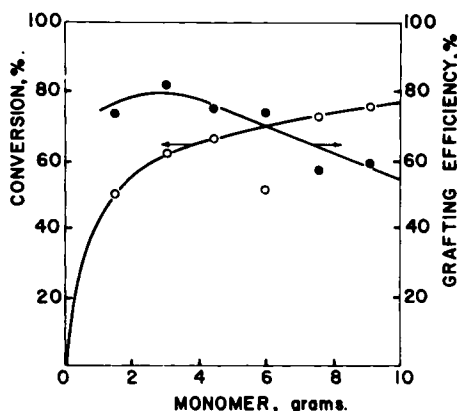| Sample	Monomer, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Molecular weight of copolymer
89	1.51	50.0	17.4	73.6	19,500
72	3.03	62.0	35.6	82.1	18,500
71	4.46	66.5	51.4	75.1	28,000
68	5.98	51.7	52.8	74.2	24,500
67	7.57	73.0	72.9	57.3	18,500
60	9.09	76.0	92.3	59.1	17,000

[a] 18 Hours of reaction time.

Fig. 5. Effect of monomer concentration on total conversion and on grafting efficiency.

This phenomenon is probably due to a greater rate of incidence of chain transfer by monomer. Such type of transfer causes a formation of homopolymer in the system unless an immediate transfer back to the backbone material can take place. The latter process will be promoted by a higher pulp:monomer ratio, and better grafting efficiency is therefore expected at low monomer concentrations.

The molecular weight of the copolymerized acrylonitrile (Fig. 6) does not undergo any spectacular change in the monomer concentration investigated. Except for the two middle points, the molecular weights would appear to remain almost constant. There is, however, a distinct possibility of a maximum on the molecular weight-versus-monomer concentration curve with regard to the chain transfer considerations brought up above.

Although most of the experiments compiled in this article were carried out at 25°C, a few experiments have been done to ascertain the role of the temperature parameter in the xanthate grafting reaction. The grafting results obtained at three different temperatures are shown in Table VI. It is evident that the effect of temperature is small, if any. One should

TABLE VI
Effect of Temperature on Grafting[a]

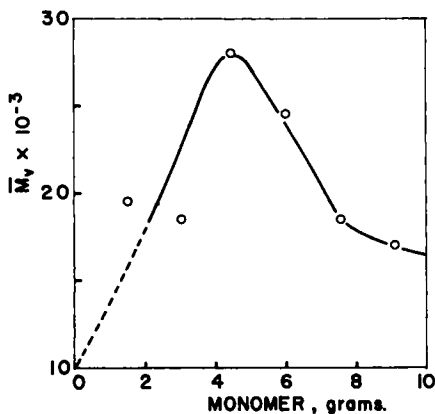| Sample	Temperature, °C	Total conversion, %	Polymer loading, %	Grafting efficiency, %
57	25	75.0	98.3	62.6
55	35	79.3	89.1	55.8
56	40	83.1	99.5	59.5

[a] 18 Hours of reaction time.

Fig. 6. Copolymer molecular weight as a function of monomer concentration.

note, however, that these results have been obtained at 18 hr of reaction time. At the end of that period, the system is already inactive and the grafting parameters found are the final ones and represent average values over the whole reaction period. It is conceivable that greater changes could be observed if the reactions were terminated at an earlier time (1–2 hr). It is the authors' opinion, however, that temperature is not as important in this reaction as some other factors discussed earlier, and the temperature of 25°C was chosen for the sake of convenience and easy application.

The experiments discussed above have been carried out in an aqueous medium. There were some indications in the literature, however, that grafting might be promoted by the presence of certain organic solvents. For example, Quéré and co-workers[12] have found that the presence of tert-butyl alcohol or acetone considerably improved grafting efficiency in the case of acrylamide grafting onto cellulose, initiated by ceric nitrate. It appeared of interest to find out whether or not similar effects could be encountered in the present system. Table VII summarizes the relevant results obtained with five organic solvents of varying chemical structure and polarity.

The total conversion data shown in Table VII indicate a negative effect regardless of the type of solvent used. A drastic reduction in total con-

TABLE VII
Effect of the Presence of Organic Solvents on Grafting[a]

Sample	Solvent	Total conversion, %	Polymer loading, %	Grafting efficiency, %
49	—	39.9	51.9	61.6
85	Methanol	22.2	25.3	54.4
84	Acetone	14.7	23.1	75.2
81	Isopropyl alcohol	10.8	5.7	26.4
82	Isobutyl alcohol	15.9	26.6	79.8
83	tert-Butyl alcohol	24.2	40.7	80.4

[a] Conditions: 1 hr reaction time; solvent:water = 1:2 (by volume).

version is recorded especially with acetone, isopropyl alcohol, and isobutyl alcohol. In the case of isopropyl alcohol, this is combined with a profound decrease in grafting efficiency, most likely due to chain transfer caused by this agent. On the other hand, acetone, isobutyl alcohol, and tert-butyl alcohol raise the grafting efficiency in accordance with the data reported by Quéré et al.[12] The influence of these reagents thus appears to be more general and probably applies to other (initiator–monomer substrate) systems as well. In view of the substantial drop of total conversion and of the high cost of such organic solvents in comparison with water, it is doubtful that their use to improve the grafting efficiency would be ecomically justified. This is even more true in the case of the xanthate grafting method, where a satisfactory grafting efficiency may be obtained by other, less expensive, means.

CONCLUSIONS

Among the factors investigated, there are two which exert a marked effect on the grafting reaction: the pH of the reaction mixture and the concentration of hydrogen peroxide. By varying these two factors, one can optimalize the process so the most advantageous relation between total conversion and grafting efficiency may be obtained. Graft copolymers virtually free of homopolymers can be prepared by using a peroxide concentration of about 20 g/l. The molecular weight of copolymers obtained under those conditions is sufficiently low to ensure efficient modification of a substrate material with the least amount of polymer grafted. Moreover, polymer loading and molecular weight can be easily controlled by a simple change in the reaction parameters.

It is evident that the results of these investigations made with a specific monomer–substrate pair cannot be immediately extended to other systems without need for further experimentation. Nevertheless, experiments carried out in this laboratory with other pulps and monomers clearly indicate that the present results have a broader validity in that they can be used to predict the copolymerization behavior of other systems.

The subject matter treated in this paper forms part of the general research program of the Groupe de Recherche en Pâtes et Papiers at this University.

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