

The Xanthate Method of Grafting. VI. The Copolymer-Homopolymer Ratio

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Synopsis

Wood pulp was copolymerized with butyl acrylate as monomer. The xanthate redox method was employed to initiate the reaction. The effect of reaction time and temperature on the relative yield of grafted polymer and homopolymer was investigated. In the lower temperature region (15°–25°C), induction periods ranged from 10 to 30 min. No induction periods were observed at higher temperatures (40° and 60°C). The copolymer/homopolymer ratio was found to depend on both time and temperature. A considerable amount of homopolymer was formed in the initial stage of the reaction. Increased reaction temperature resulted in lower grafting efficiency. Similarly, both graft and homopolymer molecular weights decreased with rising reaction temperature.

INTRODUCTION

Grafting as a technique for the modification of both natural and synthetic polymeric materials has been investigated for a number of years. Cellulose has been one of the most frequently used backbone materials, and corresponding work has resulted in a great number of patents and publications. Several excellent review articles have also been published on the subject.¹⁻⁴

Ideally, the product of a graft copolymerization should contain no homopolymer. The presence of homopolymer in the reaction product usually has a negative effect on its properties. Furthermore, the formation of homopolymer reduces possible copolymer yield, and a costly extraction procedure may be necessary to remove it from the products. Unfortunately, all graft copolymerization methods give rise to some polymer which is not chemically bound to the substrate. Its relative amount depends on different factors such as the type of cellulosic material used, the type of initiator, the type of monomer, as well as on the reaction conditions employed (temperature, concentration of reactants).

The xanthate method of grafting, discovered by Faessinger and Conte,⁵ appears to offer considerable advantages over other grafting processes. With pure cellulosic substrates, it has been shown to yield relatively minor amounts of homopolymers.^{6,7} When using wood pulps, however, the results vary and are influenced by the residual lignin and hemicellulose. Results published by the

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present authors⁸ demonstrate that, on the one hand, copolymers almost free of homopolymers could be prepared with bleached Kraft pulps⁸ (lignin content $\leq 0.05\%$); and, on the other hand, reaction products obtained under the same reaction conditions with mechanical pulp⁹ (lignin content = 27%) contained more than 50% homopolymer. Former experiments carried out with a Kraft semi-bleached pulp¹⁰ (lignin content = 0.8%) gave a clear indication that even the very low amount of lignin present led to a diminished grafting efficiency. However, the amount of homopolymers could be easily reduced in the presence of a higher concentration of hydrogen peroxide as coinitiator. From a more practical point of view, it appears that such a way of increasing grafting efficiency would be too expensive, even after discounting the fact that high concentrations of H_2O_2 considerably reduce the mechanical properties of the pulp. Furthermore, this method of increasing grafting efficiency does not work with high-lignin pulps.⁹

The aim of the present paper is to find out more about the rate of polymer formation in the xanthate grafting system, in particular, as regards the parallel formation of grafted polymer and homopolymer and as regards their respective molecular weights.

EXPERIMENTAL

Materials

Kraft semibleached pulp (lignin content = 0.8%) has been used throughout this work as a grafting substrate. It was supplied by the Consolidated-Bathurst Company, Division Waygamack.

Butyl acrylate (Eastman) was distilled on a column filled with copper rings. The center cut was collected and stored in a refrigerator.

All other reagents used in this work were employed as supplied by the manufacturers.

Copolymerization

The technique of pulp preconditioning as well as the copolymerization conditions have been described in previous papers.^{10,11} The degree of xanthation of the pulp was determined by iodometry. The value found was $\gamma = 5.0 \pm 0.4$. All experiments discussed in this article were carried out using conditions as follow: pulp, 4.5 g \pm 0.01 g (oven-dry weight of never-dried pulp); monomer (butyl acrylate), 9.00 g; water, 450 ml; surfactant (Tween-40), 0.9 g; H_2O_2 , 1.5 g (diluted into 25 ml before adding). The polymerization was terminated by additions of hydroquinone. Excess hydrogen peroxide was destroyed by treating the products with 1% $K_2S_2O_5$ solution.

Extraction

The quantity of homopolymer in the reaction products was determined by a 12-hr Soxhlet extraction of 2–3-g samples of the products with acetone. The calculations concerning the grafting parameters were made considering the loss of pulp during mercerization due to its solubility in NaOH (about 3.5%).

The grafting parameters are defined as follows:

$$\text{total conversion, \%} = (D - B)/C \times 100,$$

$$\text{polymer loading, \%} = (A - B)/B \times 100,$$

$$\text{grafting efficiency, \%} = (A - B)/(D - B) \times 100$$

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

Grafted Polymer. Grafted poly(butyl acrylate) was isolated by hydrolyzing away the cellulose with 72% sulfuric acid according to the procedure described by Nakamura and co-workers,¹² followed by dissolving the residue in acetone and filtration.

Homopolymer. Poly(butyl acrylate) homopolymer was isolated by shaking dry reaction products with acetone during 3 hr. The clear solution of homopolymer was collected.

In both cases, viscosity was recorded at 25°C in acetone at four different concentrations in Ubbelohde viscometers. Following extrapolation to obtain the intrinsic viscosity $[\eta]$, the corresponding degree of polymerization was calculated according to the expression¹²

$$[\eta] = 5.53 \times 10^{-3} \times P^{0.66}$$

Polymer molecular weight was obtained by multiplying the degree of polymerization P by monomer molecular weight.

RESULTS AND DISCUSSION

While a previous work¹⁰ on the effects of reaction conditions on xanthate grafting used acrylonitrile as monomer, the present work was carried out with butyl acrylate. Preliminary experiments had indicated that copolymerizations with butyl acrylate as monomer resembled closely those with acrylonitrile, with the exception that the reaction rate was considerably higher with the former. This is an important factor: the heterogeneous character of the reaction makes it impossible to withdraw well-defined samples. Therefore, each point on the

TABLE I
Dependence of Grafting on Reaction Time at 15°C

Sample no.	Time, min	Conversion, %			Polymer loading, %	Grafting efficiency, %
		Homo-polymer	Grafted polymer	Total		
159	5	—	—	0	—	—
158	10	—	—	0	—	—
157	20	—	—	0	—	—
155	30	—	—	0	—	—
185	40	24.6	13.7	38.3	27.1	35.9
153	50	15.0	37.1	52.1	74.3	71.3
161	60	16.5	40.6	57.1	81.1	71.1
160	120	20.3	46.0	66.3	92.0	69.4

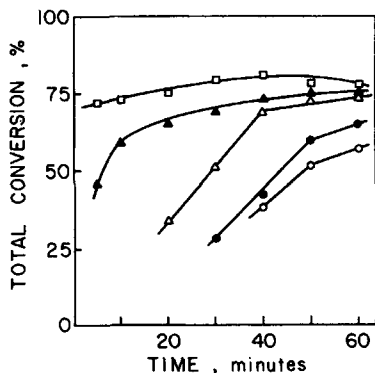


Fig. 1. Total conversion to polymer as a function of reaction time and temperature: (O) 15°C; (●) 20°C; (Δ) 25°C; (▲) 40°C; (□) 60°C.

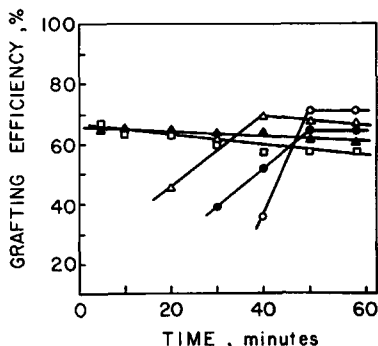


Fig. 2. Grafting efficiency as a function of reaction time and temperature: (O) 15°C; (●) 20°C; (Δ) 25°C; (▲) 40°C; (□) 60°C.

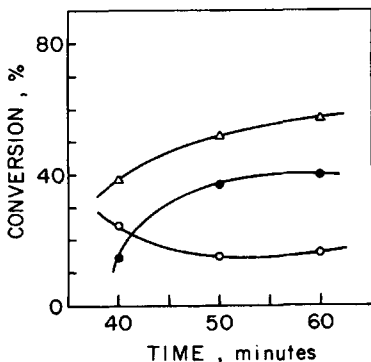


Fig. 3. Copolymer-homopolymer composition of products formed at 15°C: (O) homopolymer; (●) grafted polymer, (Δ) total polymer.

conversion curve must be obtained by a separate experiment. This permits one to obtain enough sample to determine the copolymer-homopolymer ratio (grafting efficiency) and to measure the molecular weights.

Experiments were carried out at five different temperatures (15°–60°C), with reaction times ranging from 5 min to 2 hr. The data obtained, including total conversion, conversion to grafted polymer, conversion to homopolymer, polymer loading, and grafting efficiency, have been compiled in Tables I–V.

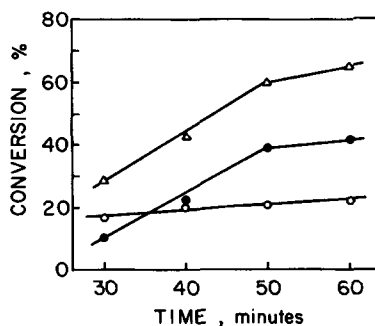


Fig. 4. Copolymer-homopolymer composition of products formed at 20°C: (O) homopolymer; (●) grafted polymer; (Δ) total polymer.

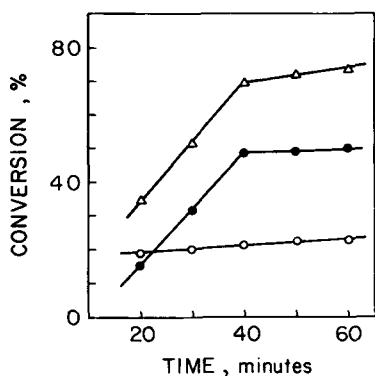


Fig. 5. Copolymer-homopolymer composition of products formed at 25°C: (O) homopolymer; (●) grafted polymer; (Δ) total polymer.

Figure 1 plots total conversion to polymer as a function of time. The five curves obtained demonstrate the strong effect of temperature on the polymerization. Apart from the normal increase of conversion with rising temperature, the data obtained at the three lower temperatures show rather long induction periods. It is, therefore, clear that it is in particular the initiation reaction which is influenced by reaction temperature. At 60°C, one obtains a very high conversion already at 5 min reaction time, which increases only slightly thereafter.

TABLE II
Dependence of Grafting on Reaction Time at 20°C

Sample no.	Time, min	Conversion, %			Polymer loading, %	Grafting efficiency, %
		Homo-polymer	Grafted polymer	Total		
149	5	—	—	0	—	—
147	10	—	—	0	—	—
148	20	—	—	0	—	—
179	30	17.2	11.1	28.3	22.5	39.1
144	40	20.3	22.1	42.4	44.3	52.2
145	50	21.1	38.9	60.0	77.9	64.9
143	60	23.3	42.1	65.4	84.1	64.3
142	120	20.7	47.0	67.7	93.9	69.4

Similarly at 40°C, the 5-min conversion is quite high (46.4%). Another 15°C drop in temperature, however, gives a system which shows no polymer formation up to 10 min of reaction time. This induction period increases in a regular manner with a further drop in temperature, attaining 20 min and 30 min at 20°C and 15°C, respectively. (The duration of the induction periods is taken as the longest reaction time used which produces no polymer. The true induction periods could be longer by several minutes.) On the other hand, the overall rate of polymerization as estimated from the slopes of the corresponding conversion curves, seems to be much less influenced by the temperature. In all cases, the reaction stops at 60–80% conversion, beyond which polymer formation ceases.

The appearance of induction periods when grafting a vinyl monomer onto wood pulp is not surprising. Previous work⁸ involving a series of partially delignified Kraft pulps and acrylonitrile as monomer has indicated the presence of induction periods even with relatively low-lignin pulps (0.6–1.0%). Similar effects have been reported for other grafting systems. During a ceric nitrate-initiated grafting of acrylonitrile with Kraft pulps, Erdelyi¹⁴ observed induction periods which varied from 1 min to 12 min according to the lignin content in the pulp. On the contrary, experiments carried out by Dimov and Pavlov, employing very pure xanthated cellulose (partially hydrolyzed viscose) with acrylonitrile as the monomer and H₂O₂ as the coinitiator, have not shown any induction periods. A similar behavior was reported by Samoylov and co-workers,¹⁵ who investigated grafting initiated by the reaction between the xanthate groups of partially hydrolyzed viscose and pentavalent vanadium (HVO₃).

More important than the total conversion is the percentage of polymer that is truly grafted to the backbone material (grafting efficiency). All grafting techniques produce more or less homopolymer beside the main product. Its relative amount depends on various factors such as the character of the grafting substrate and of the monomer, the nature of the initiating system, etc.

It is indeed true that no grafting system precludes completely the formation of unattached polymer. Considering the example of the [cellulose xanthate/hydrogen peroxide] initiating system, one observes that ungrafted polymer chains may be started by ·OH radicals:

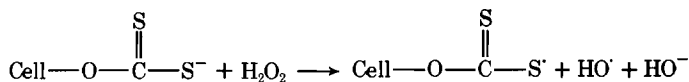


TABLE III
Dependence of Grafting on Reaction Time at 25°C

Sample no.	Time, min	Conversion, %			Polymer loading, %	Grafting efficiency, %
		Homo-polymer	Grafted polymer	Total		
91	5	—	—	0	—	—
183	10	—	—	0	—	—
176	20	18.8	15.7	34.5	31.1	45.5
184	30	20.0	31.8	51.8	63.6	61.4
173	40	21.3	48.4	69.7	96.6	69.4
172	50	23.2	49.0	72.2	98.0	67.9
171	60	23.9	49.9	73.8	99.8	67.6
169	120	19.3	56.5	75.8	113.0	74.5

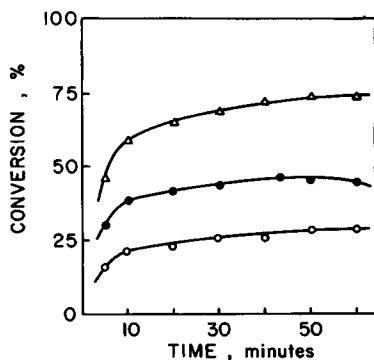


Fig. 6. Copolymer-homopolymer composition of products formed at 40°C: (O) homopolymer; (●) grafted polymer; (Δ) total polymer.

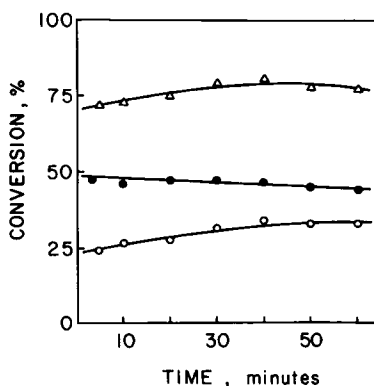
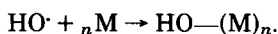
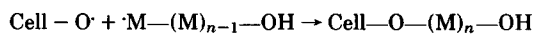


Fig. 7. Copolymer-homopolymer composition of products formed at 60°C: (O) homopolymer; (●) grafted polymer; (Δ) total polymer.



However, growing homopolymer radicals may become copolymers by a recombination with radicals present on the backbone:



A mechanism has also been proposed by Gaylord¹⁶ by which graft copolymerization results from termination of growing polymer chains on cellulose by insertion into aldehyde groups.

TABLE IV
Dependence of Grafting on Reaction Time at 40°C

Sample no.	Time, min	Conversion, %			Polymer loading, %	Grafting efficiency, %
		Homo-polymer	Grafted polymer	Total		
132	5	15.9	30.5	46.4	61.0	65.8
131	10	20.7	38.8	59.5	77.5	65.2
130	20	23.1	42.4	65.5	84.8	64.7
128	30	25.6	44.1	69.7	88.2	63.2
129	40	25.9	47.3	73.2	94.4	64.6
127	50	28.4	46.7	75.1	93.3	62.2
126	60	29.4	45.7	75.1	91.4	60.9

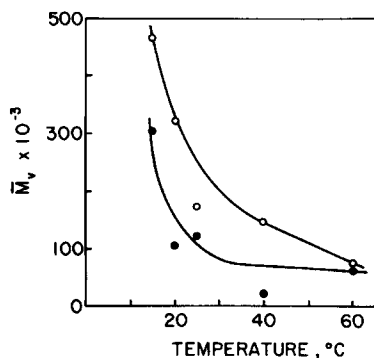


Fig. 8. Homopolymer and graft molecular weight as a function of reaction temperature: (O) homopolymer; (●) grafted polymer; reaction time 60 min.

Previous work¹⁰ has shown that with acrylonitrile as a monomer, the grafting efficiency observed was mostly about 60–70%. Similar results have been obtained with other monomers (styrene, methyl methacrylate, ethyl acrylate). Figure 2 shows the dependence of grafting efficiency on time and temperature in the present system. It is evident that, once again, most grafting efficiency values are situated in the neighborhood of 60%. This relative independence of homopolymer content of the nature of the monomer would indicate that it is rather the character of the backbone material which has the decisive effect on the reaction. Much greater changes in grafting efficiency were observed when using different pulps as substrates.^{8,9}

TABLE V
Dependence of Grafting on Reaction Time at 60°C

Sample no.	Time, min	Conversion, %			Polymer loading, %	Grafting efficiency, %
		Homo-polymer	Grafted polymer	Total		
139	5	24.1	47.9	72.0	95.7	66.5
138	10	26.8	46.3	73.1	92.7	63.4
137	20	27.5	47.3	74.8	94.7	63.3
136	30	31.6	47.7	79.3	95.3	60.2
135	40	34.6	46.7	81.3	93.4	57.5
134	50	33.1	45.0	78.1	89.9	57.6
133	60	33.4	44.3	77.7	88.5	57.0

TABLE VI
Dependence of Polymer Molecular Weight on Reaction Time at 15°C

Sample no.	Time, min	Intrinsic viscosity [η]		Molecular weight $\bar{M}_v \times 10^{-3}$	
		Homo-polymer	Grafted polymer	Homo-polymer	Grafted polymer
185	40	1.630	0.593	707	153
153	50	1.467	0.765	603	225
161	60	1.241	0.936	468	305
160	120	1.022	1.034	348	355

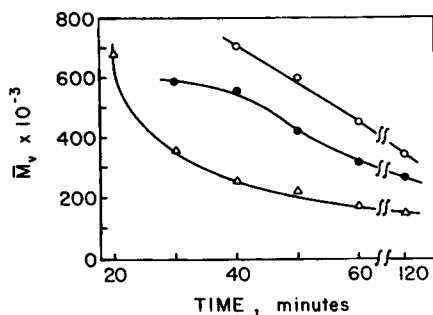


Fig. 9. Homopolymer molecular weight as a function of reaction time and temperature: (O) 15°C; (●) 20°C; (Δ) 25°C.

The data plotted in Figure 2 also show that, in general, grafting efficiency increases with decreasing temperature. At the three lower temperatures (15°, 20°, and 25°C), grafting efficiency increases with time, especially in the first phases of the reaction. At 40° and 60°C, however, slight decrease in grafting efficiency occurs with increasing reaction time. The behavior of the system is better illustrated in Figures 3–7, which compare the total conversion with the conversion to homopolymer and with the conversion to grafted polymer at each of the five temperatures studied.

Let us discuss these plots in the ascending order of temperature: At 15°C (Fig. 3), the homopolymer content in the product seems to decrease slightly with time, while the increase in total conversion is accounted for wholly by the formation

TABLE VII
Dependence of Polymer Molecular Weight on Reaction Time at 20°C

Sample no.	Time, min	Intrinsic viscosity $[\eta]$		Molecular weight $\bar{M}_v \times 10^{-3}$	
		Homopolymer	Grafted polymer	Homopolymer	Grafted polymer
179	30	1.441	0.308	587	57
144	40	1.398	0.659	560	179
145	50	1.158	0.580	421	148
143	60	0.971	0.468	322	107
142	120	0.860	0.376	268	76

TABLE VIII
Dependence of Polymer Molecular Weight on Reaction Time at 25°C

Sample no.	Time, min	Intrinsic viscosity $[\eta]$		Molecular weight $\bar{M}_v \times 10^{-3}$	
		Homopolymer	Grafted polymer	Homopolymer	Grafted polymer
176	20	1.588	0.659	680	179
184	30	1.050	0.739	363	213
173	40	0.847	0.695	262	194
172	50	0.768	0.671	226	184
171	60	0.649	0.507	175	121
169	120	0.603	0.419	157	90

of grafted polymer. A similar situation is found at 20°C (Fig. 4) and 25°C (Fig. 5). While the homopolymer content increases slowly up to 60 min of reaction time, it drops again at 120 min (Tables II and III); the bulk of the increase in total conversion is, therefore, once again explained by the formation of grafted polymer. The picture changes at 40°C where both types of polymer show a net increase of an approximately equal magnitude (Fig. 6). Finally, at 60°C (Fig. 7), the amount of copolymer decreases with time while more homopolymer is formed.

The five sets of data discussed in the previous paragraph have one feature in common: the relatively high percentage of homopolymer formed in the beginning of the reaction. It appears that, regardless of whether or not there is an induction period, the first nonzero conversion experiment (40 min at 15°C, 30 min at 20°C, etc.) gives always approximately 20% yield of homopolymer. Under the same conditions, the yield of grafted polymer varies between 11.1% and 47.9%. It is difficult to account for this phenomenon. As a possible explanation, one could conceive of a reaction between hydrogen peroxide and an impurity in the pulp (e.g., residual degraded lignin), which could occur before the onset of the main reaction between hydrogen peroxide and cellulose xanthates and give rise to the formation of homopolymer during the first stages of the process.

The decrease of grafting efficiency with time at the two higher temperatures (40° and 60°C) may be explained by the gradual depletion of xanthate groups available for the initiation reaction. Increased formation of homopolymers in later stages of the reaction at higher temperatures (40° and 50 °C) has also been reported by Dimov and Pavlov. However, greater frequency of chain transfer by monomer could also account for the lower grafting efficiency observed at higher temperatures, especially if this decrease were accompanied by a simultaneous decrease of molecular weight of the polymer formed.

This is clearly the case with the homopolymers, as evidenced by the molecular weight data listed in Tables VI–IX. At 60 min of reaction time, for example, the 15°C molecular weight is 468,000; it decreases gradually to 89,000 at 60°C (Fig. 8). Results obtained with the other reaction times follow a similar pattern. The most probable explanation for this decrease of homopolymer molecular weight with temperature would be an increased rate of chain transfer at higher temperatures.

It has been shown in a previous paper¹⁰ that homopolymer molecular weight

TABLE IX
Molecular Weights at 40° and 60°C

Sample no.	Time, min	Temperature, °C	Intrinsic viscosity [η]		Molecular weight $\bar{M}_v \times 10^{-3}$	
			Homopolymer	Grafted polymer	Homopolymer	Grafted polymer
127	50	40	0.613	0.183	160	25
126	60	40	0.569	0.166	144	22
134	50	60	0.273	0.165	47	22
133	60	60	0.414	0.316	89	59

decreased rapidly with reaction time. This effect is also evident in the present work. The plots shown in Figure 9 illustrate the abrupt character of this decrease which is the more rapid the higher the temperature. Because of the complexity of the reaction system, it is difficult to find a satisfactory explanation for this effect. It is possible that hydrogen peroxide reacts with some components of the pulp producing compounds effective as chain transfer agents. The concentration of such agents would rise with time, thus reducing molecular weight of the polymers formed.

Molecular weights of the grafted polymer are also listed in Tables VI-IX. It is evident that they show a much greater variation. This is believed to be mainly due to the fact that the process of hydrolyzing away cellulose with 72% sulfuric acid also causes some hydrolysis and degradation of the butyl acrylate polymer. Attempts to apply the acetic acid-acetic anhydride method described by Rogovin and co-workers¹⁸ failed, most likely due to a complete transesterification of poly(butyl acrylate) leading to the formation of water-soluble poly(acrylic acid). Nevertheless, Figure 8 shows that at 60 min, molecular weight of copolymerized poly(butyl acrylate) also seems to decrease substantially with increasing reaction temperature. A similar decrease is also evident at 50 and 120 min of reaction time; experiments stopped at 40 min, and at 30 min they show a certain increase of molecular weight with rising temperature. At all times, however, graft molecular weight is lower than that of the homopolymer. A similar effect has been observed in a previous work¹⁰ with acrylonitrile as a monomer; it can be explained by the fact that, unlike the homopolymer, grafted chains grow solely in the vicinity of cellulose (or other pulp components), hence a greater probability of chain transfer to the backbone material will exist.

The molecular weights of grafted poly(butyl acrylate) found in this work are much higher than those observed with polyacrylonitrile.^{10,15} Consequently, the efficiency of modification obtained with the same polymer loading would be lower in the present case. While an attempt was made to test the papermaking properties of the copolymerized pulps, it was found impossible to disintegrate them sufficiently to make a homogeneous slurry. Nakamura and co-workers¹² reported that rather extensive crosslinking occurred in the graft copolymerization of cellulose with ethyl acrylate. This may also be the case in the present work, partly explaining the greater variation of graft molecular weights.

References

1. V. T. Stannett and H. B. Hopfenberg, in *Cellulose and Cellulose Derivatives*, N. Bikales and L. Segal, Eds., Vol. 5, Part 5, Wiley, New York, 1970, pp. 907-936.
2. J. C. Arthur, *Adv. Macromol. Chem.*, **2**, 1 (1970).
3. M. S. Bains, *J. Polym. Sci. C*, **No. 37**, 125 (1972).
4. K. Ward, Jr., *Chemical Modification of Papermaking Fibers*, Marcel Dekker, New York, 1973, pp. 167-215.
5. R. W. Faessinger and J. S. Conte, U.S. Pat. 3,359,224 (Dec. 9, 1967); U.S. Pat. 3,330,787 (July 11, 1967).
6. W. J. Brickman and R. W. Faessinger, *Text. Chem. Color.*, **5**, 38 (1973).
7. K. Dimov and P. Pavlov, *J. Polym. Sci. A-1*, **7**, 2775 (1969).
8. V. Hornof, B. V. Kokta, and J. L. Valade, *J. Appl. Polym. Sci.*, **19**, 1573 (1975).
9. V. Hornof, V. V. Kokta, and J. L. Valade, *J. Appl. Polym. Sci.*, **20**, 1543 (1976).

10. V. Hornof, B. V. Kokta, and J. L. Valade, *J. Appl. Polym. Sci.*, **19**, 545 (1975).
11. B. V. Kokta and J. L. Valade, *Tappi*, **55**, 366 (1972).
12. Y. Nakamura, J. C. Arthur, Jr., M. Negishi, K. Doi, E. Kageyama, and K. Kudo, *J. Appl. Polym. Sci.*, **14**, 929 (1970).
13. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1967.
14. J. Erdélyi, *Zellstoff Papier*, **8**, 243 (1970).
15. V. I. Samoylov, B. P. Morin, and Z. A. Rogovin, *Faserforsch. Textiltech.*, **22**, 297 (1971).
16. N. Gaylord, *J. Polym. Sci. C*, **37**, 153 (1972).
17. V. Hornof, C. Daneault, B. V. Kokta, and J. L. Valade, to be published.
18. A. A. Gulina, R. M. Livshits, and Z. A. Rogovin, *Vysokomol. Soedin.*, **7**(9), 1529 (1965).

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