Thermal Behavior of Graft Copolymers of Cotton Cellulose and Acrylate Monomers

D. S. VARMA and VEENA NARASIMHAN, *Indian Institute of Technology, Delhi, New Delhi-29, India*

Synopsis

Cotton cellulose yarn was grafted with methyl acrylate, ethyl acrylate, n-butyl acrylate, and methyl methacrylate at various percentages of grafting. The effects of concentration of the initiator, concentration of the acid, and of temperature on grafting was studied and the mechanism discussed. The effect of reactivity of the monomer on the percentage graft-on is pointed out. Thermal behavior of natural and grafted cotton yarn was studied using dynamic thermogravimetry in air at a heating rate of 6°C/min up to a temperature of 500°C. The thermal stabilities of the samples grafted with various acrylate monomers to various percentages of grafting were computed from their primary thermograms by calculating the values of *IDT*, *IPDT*, and *E**. The results show that the thermal stability increases with increase in graft-on per cent, and the thermal stabilities of natural cotton and cotton grafted with different monomers are in the order ethyl > methyl > natural cellulose > methyl methacrylate > n-butyl acrylate.

INTRODUCTION

Modification of cellulose fibers by graft copolymerization with various monomers is considered to be very effective in bringing about desired changes in the properties of cellulose fibers. Of these, the vinyl monomers have received much greater attention than others. Kaizerman et al.,[1] Negishi and co-workers,[2] Hebeish and Mehta,[3] among a host of other investigators, have grafted vinyl monomers on cellulose using ceric ion as initiator. While they attempted to graft copolymerize cellulose to various degrees of substitution and also carry out certain physical studies, they did not test the thermal stability of the grafted fibers. Many workers have studied the pyrolysis of cellulose and modified cellulose[4–9] but not the thermal behavior of cellulose grafted with acrylic monomers. Hurduc et al.[10] very recently investigated the thermal behavior of cotton cellulose grafted with methyl acrylate, methyl methacylate, etc. They found that the thermal stability of cellulose grafted with acrylic monomers is lower than that of the initial cellulose.

In view of the great importance of thermal stability of cotton cellulose, a systematic investigation of the thermal behavior of cotton cellulose grafted with ethyl acrylate, n-butyl acrylate, methyl acrylate, and methyl methacrylate was undertaken by us. In this communication we report our

results on optimizing the conditions of grafting, using ceric ion as an initator, and the thermogravimetric analysis of the grafted samples. Thermal stabilities of these grafted samples are compared from their integral procedural decomposition temperatures as proposed by Doyle.[11] The kinetics or thermal degradation of these grafted samples have been investigated to understand the energetics of the degradation reaction.

EXPERIMENTAL

Materials

Bleached California cotton yarns (5[s], Tpi = 3) which were extracted with methanol for 4 hr to remove greasy matter were used. The BDH reagent-grade monomers were freed from the inhibitor and were distilled before use. Baker analyzed reagent-grade ceric ammonium nitrate and other BDH laboratory reagent-grade chemicals were used for grafting.

Graft Copolymerization of Cotton Cellulose

Graft copolymerization was carried out in a three-necked flask in nitrogen atmosphere. Dried cotton hanks were immersed in a solution consisting of nitric acid ($0.25N$ to $1.0N$) and ceric ammonium nitrate ($0.001N$ to $0.04N$) at temperatures from 30°C to 50°C. The monomer, 5 cc, was added to the reaction mixture, and the contents of the flask were constantly stirred maintaining an atmosphere of nitrogen throughout the course of the reaction. Material-to-liquor ratio was 1:50, and the reaction time varied from 15 min to 6 hr. After the reaction has proceeded for a desired interval of time, the cotton hanks were removed and washed well with water and soap, methanol, and finally with acetone or benzene. Then the cotton hanks were left in benzene or acetone for 24 hr and then Soxhlet extracted with benzene or acetone till the homopolymer was completely removed. They were dried in an oven at 50°C, cooled to room temperature, and weighed. The grafting was calculated as the per cent increase in weight over the original weight of the samples.

TABLE I
Effect of Nitric Acid Concentration on Percentage Weight Increase[a]

Expt. no.	Concentration of HNO₃, N	Increase in weight, %
1	0.25	85
2	0.5	55
3	0.75	25.5
4	1.0	18.25

[a] Concentration of CAN in bath = $0.0075N$; concentration of monomer = 5%; time = 4 hr; temperature = 30°C; fabric-to-liquor ratio = 1:50.

Dynamic Thermogravimetric Analysis

The thermogravimetric analysis was done using a Stanton Model HT-D thermobalance in air. The yarns were cut into approximately $1/16$-in. lengths and 46 ± 5-mg samples were taken for each analysis. The analysis was carried out in air from room temperature to 500°C at a heating rate of 6°C/min. Primary thermograms were obtained by plotting per cent residual weight against temperature.
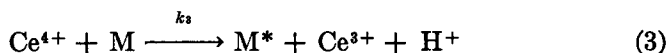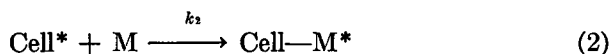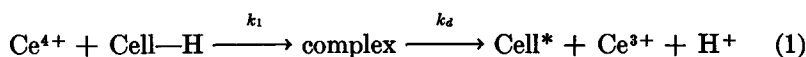
RESULTS AND DISCUSSION

Optimization of the Conditions for the Grafting of Methyl Acrylate on Cellulose
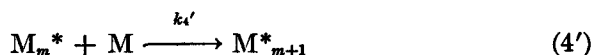
Effect of Acid Concentration on Grafting

The effect of acid concentration on the grafting of methyl acrylate on cellulose was studied at various concentrations of nitric acid, between $0.25N$ and $1N$. Below $0.25N$ in HNO_3 concentration, ceric hydroxide precipitated out. Therefore, lower concentrations could not be tried. At acid concentrations in excess of $1N$, cellulose is very strongly attacked by the acid. Thus, the range of acid concentrations which can be employed for grafting is very limited. The results of these studies are presented in Table I, which shows that the extent of grafting decreases progressively as the acid concentration increases. Ranga Rao and Kapur[12] have obtained a similar decrease in the extent of grafting as the acid concentration increases above $0.6N$ HNO_3 when grafting acrylonitrile onto cellulose. This is understandable in the light of the mechanism of graft copolymerization. The sequence of reactions eventually leading to the graft copolymerization may be written as follows:
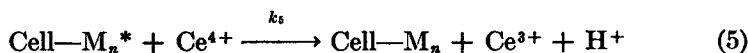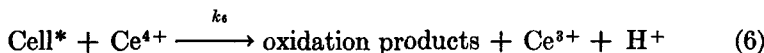
Initiation:

$$Ce^{4+} + Cell\text{—}H \xrightarrow{k_1} \text{complex} \xrightarrow{k_d} Cell^* + Ce^{3+} + H^+ \quad (1)$$

$$Cell^* + M \xrightarrow{k_2} Cell\text{—}M^* \quad (2)$$

$$Ce^{4+} + M \xrightarrow{k_3} M^* + Ce^{3+} + H^+ \quad (3)$$

Propagation:

$$Cell\text{—}M_n^* + M \xrightarrow{k_4} Cell\text{—}M^*_{n+1} \quad (4)$$

$$M_m^* + M \xrightarrow{k_4'} M^*_{m+1} \quad (4')$$

Termination:

$$Cell\text{—}M_n^* + Ce^{4+} \xrightarrow{k_5} Cell\text{—}M_n + Ce^{3+} + H^+ \quad (5)$$

$$M_m{}^* + Ce^{4+} \xrightarrow{k_5{}'} M_m + Ce^{3+} + H^+ \qquad (5')$$

$$Cell^* + Ce^{4+} \xrightarrow{k_6} \text{oxidation products} + Ce^{3+} + H^+ \qquad (6)$$
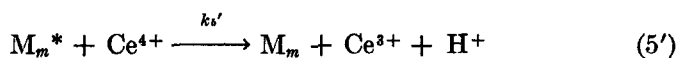
Herein are, however, included the reactions leading to homopolymer which is invariably formed as by-product of the reaction. If the graft copolymerization should proceed according to the above scheme of Ogiwara et al.,[13] the pH should have no effect on the rate of graft copolymerization. This is not borne out in our results. It is therefore likely that reactions (1), (2), and (3), which involve the formation of hydrogen ions and also the energized free radicals Cell* and M* as products, must be reversible; and, if they are, an increase in hydrogen ion concentration should suppress the initiation of the reaction. This should lead to a lowering of the extent of grafting with increased hydrogen ion concentration, as shown by the steady-state treatment in the following section.

Effect of Initiator Concentration on Grafting

Different concentrations of ceric ammonium nitrate ranging from $0.001N$ to $0.04N$ were employed in several grafting experiments, keeping the concentrations of other reagents constant. The percentage grafting increases with increasing concentration of the initiator up to $0.0075N$. Thereafter, the percentage grafting decreases as shown in Figure 1. Similar
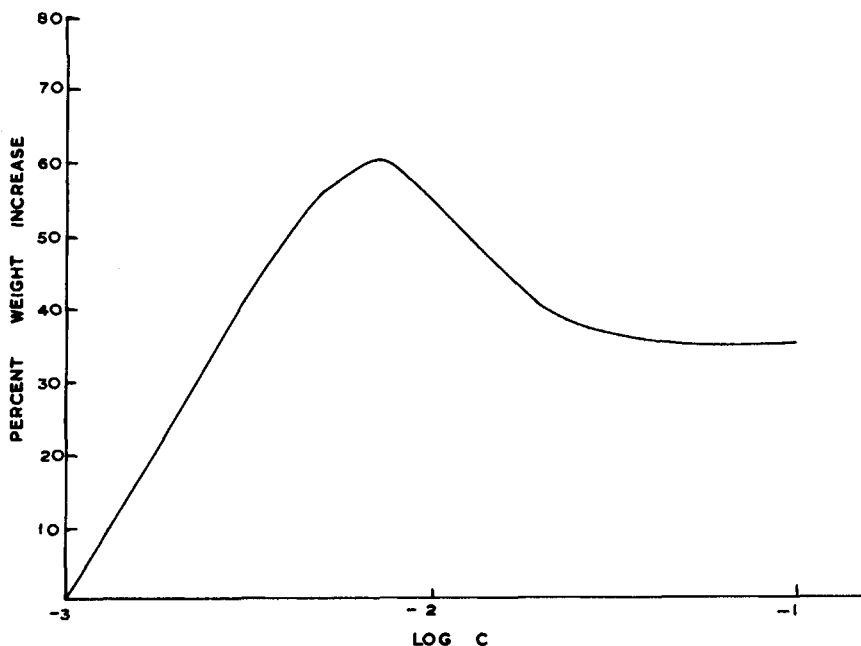

Fig. 1. Effect of concentration of the initiator on per cent increase in weight in grafting methyl acrylate onto cotton.

results were obtained by Ogiwara et al.[13] who applied a steady-state approximation to the sequence of reactions shown above. Since we are proposing a modification of that mechanism involving the reversibilities of reactions (1), (2), and (3), a new analysis is now made applying steady-state conditions. The rate of polymerization can be written as

$$R_p = \frac{k_4 k_2 [M]^2}{(k_{-2}) + k_5 [Ce^{4+}]} \left\{ \frac{k_1 [Ce^{4+}][Cell\!-\!H]}{(k_{-1})[Ce^{3+}][H^+] + k_2[M] + k_6[Ce^{4+}]} \right\}. \quad (7)$$

We will have to now consider two different cases corresponding to two different ranges of Ce^{4+} concentration.

Case 1—At low concentrations of Ce^{4+}:

$$R_p = \left\{ \frac{k_4 k_2 \, [M]^2}{k_{-2}} \frac{k_1 [Ce^{4+}][Cell\!-\!H]}{(k_{-1}) \, [Ce^{3+}] \, [H^+] + k_2[M]} \right\} \quad (8)$$

which means that the rate of polymerization R_p should increase with increase in ceric ion concentration.

Case 2—At higher concentrations of Ce^{4+} and $k_5 \gg k_4$ and k_{-2}:

$$R_p = \frac{k_4 k_2 [M]^2}{k_5 [Ce^{4+}]} \left\{ \frac{k_1 [Ce^{4+}][Cell\!-\!H]}{(k_{-1})[Ce^{3+}][H^+] + k_2[M] + k_6[Ce^{4+}]} \right\}. \quad (9)$$

Katai and co-workers[14] estimated in their studies, using ceric ion as initiator, that $k_6/k_2 = 50$. Therefore, increase in the Ce^{4+} concentration increases the magnitude of the denominator in eq. (9). Therefore, R_p should decrease with increase in Ce^{4+} concentration. A maximum per cent grafting is obtained at a particular optimum concentration of Ce^{4+}, beyond which the percentage grafting decreases progressively.

The results presented in Figure 1 show these two kinds of behavior. Since we have carried out the grafting for the same interval of time in all the cases, the per cent grafting given in Figure 1 may be taken as directly proportional to the rate of polymerization. Here we may add that the steady-state rate equation, eq. (7), also predicts a lower value of R_p at lower pH.

Effect of Temperature on Grafting

Grafting reactions were carried out at four different temperatures between 30°C and 50°C, keeping the concentrations of the reagents constant. The results are presented in Table II. The per cent grafting decreases as the temperature rises from 30°C to 50°C. A satisfactory explanation for this behavior cannot be given at this stage.

All these experiments carried out under various conditions of temperature, initiator concentration, and acid concentrations indicate that maximum grafting occurs at an initiator concentration of 0.0075N, an acid concentration of 0.25N, and a temperature of 30°C. Considering these to be the optimum conditions, the kinetics of grafting of methyl, ethyl, *n-*

TABLE II
Effect of Temperature on Percentage Weight Increase[a]

Expt. no.	Temp., °C	Increase in weight, %
1	30	85
2	40	67.76
3	45	62
4	50	63

[a] Concentration of HNO_3 in the bath = $0.25N$; concentration of monomer = 5%; time = hr; concentration of the initiator = $0.0075N$; fabric-to-liquor ratio = 1:50.

butyl acrylate and methyl methacrylate were studied under these conditions.

Grafting of Different Acrylic Monomers on Cellulose

The results of the kinetics of grafting of methyl, ethyl, n-butyl, and methyl methacrylates on cellulose yarn carried out under the optimum conditions discussed in the previous section are shown in Figure 2. The results clearly show that the number of molecules grafted onto cellulose in the case of different monomers are in the order methyl > ethyl > n-butyl > methyl methacrylate. This may be due to a decrease in the reactivity of acrylate radicals as a result of steric and polar effects. Therefore, the number of graft-on moles for the different monomers must show a linear
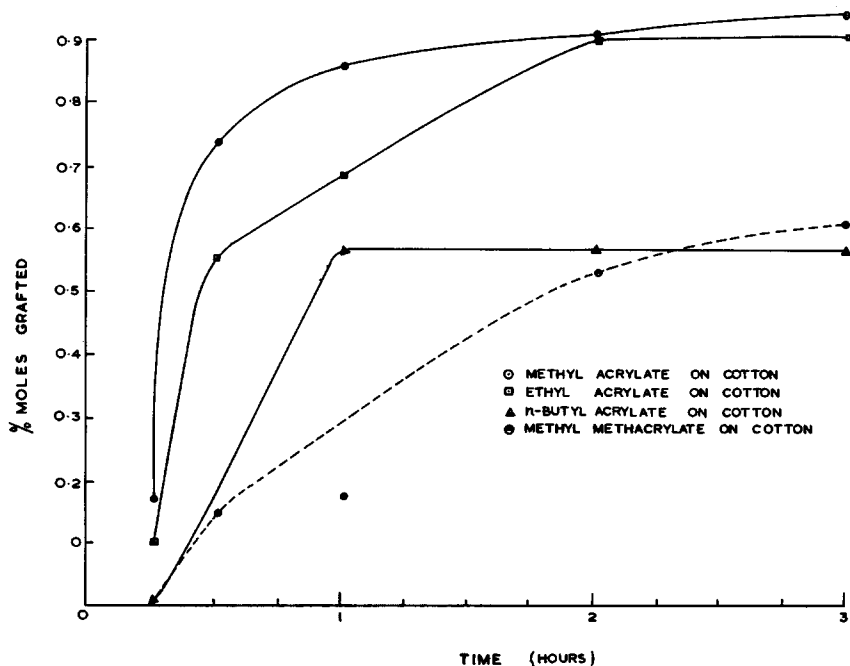

Fig. 2. Effect of time on grafting of methyl acrylate, ethyl acrylate, n-butyl acrylate, and methyl methacrylate onto cotton.
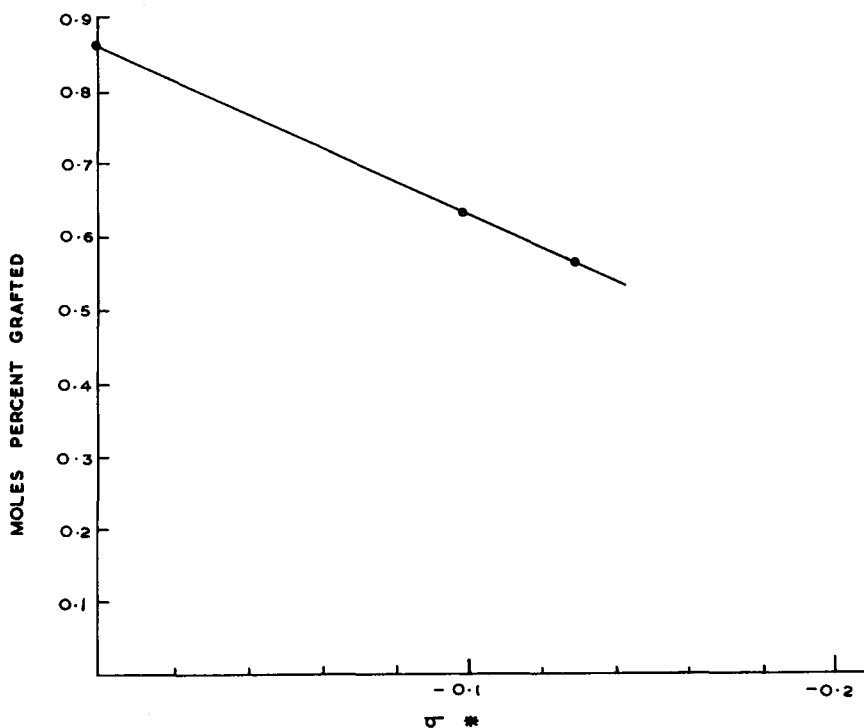
Fig. 3. Dependence on number of moles grafted on the Taft polar substituent constant of the acrylates.

dependence on the Taft polar substituent constant σ^*. Figure 3 shows that it is indeed the case.

Thermogravimetric Analysis

The thermal behavior of cotton cellulose grafted with methyl, ethyl, n-butyl, and methyl methacrylate was examined by a study of their primary thermograms. It has been reported that in the case of cotton fabrics, the loss of sorbed water is completed around 140°C.[15] The calculations of IDT, $IPDT$, and E^* were therefore carried out in the temperature range of 140°C to 500°C to understand the thermal behavior of the dried samples. The two important aspects influencing the mode of thermal degradation of these samples are (1) the percentage grafting and (2) the nature of the monomer. Primary thermograms of natural cotton and cotton grafted with acrylate monomers are shown in Figures 4 to 7. The shapes of the thermograms of natural cotton and cotton grafted with different acrylates do not differ very much from each other.

In the case of cellulose grafted with methyl acrylate to various degrees of grafting, the thermal stability of grafted cellulose is higher than that of natural cellulose up to a temperature of 350°C, as is evident from Figure 4
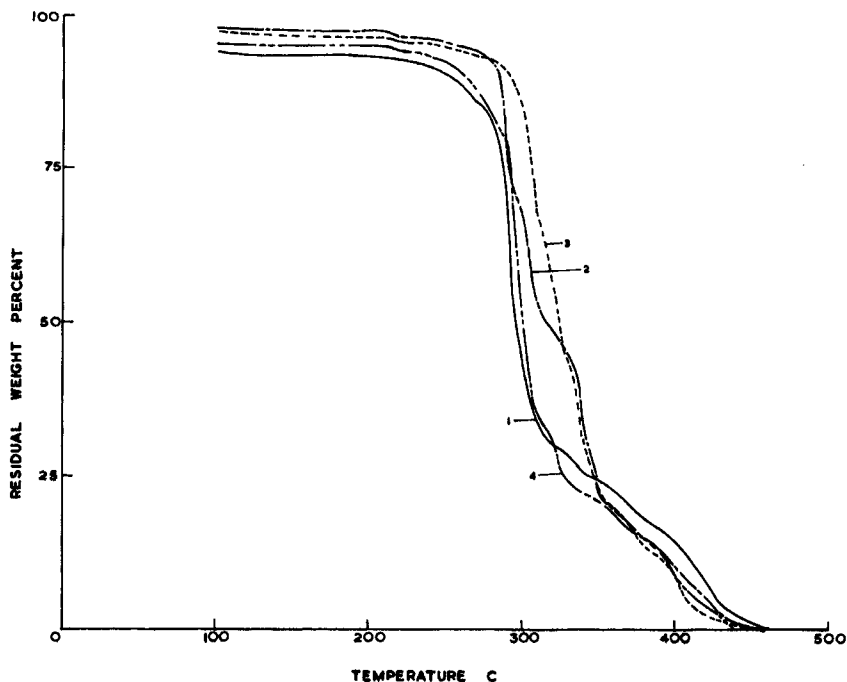
Fig. 4. Primary thermograms of natural cotton and cotton grafted with methyl acrylate: (1) natural cotton; (2) 15% graft copolymerized; (3) 62% graft copolymerized; (4) 74% graft copolymerized.

and the decomposition temperature T_D at different weight losses presented in Table III. In natural cotton, T_D at 10% decomposition is 274°C, but in samples with 15%, 62%, and 74% graft-on, the T_D values are 282°C, 298°C, and 296°C respectively. At 60% decomposition T_D for natural cotton is 300°C, and those for 15%, 62%, and 74% graft-on are 306°C, 336°C, and 338°C. In natural cotton, the main weight loss occurs between 250°C and 300°C, whereas in methyl acrylate-grafted samples, main weight loss occurs between 260°C and 330°C in 15% grafted cotton and between 270°C and 336°C in 62% and 74% grafted cottons. Hence the effect of grafting methyl acrylate onto cellulose is to make it more thermally stable up to 350°C, and this effect becomes more predominant as the percent graft-on increases. After 350°C, the grafted samples lose weight more rapidly than normal cotton, which can be explained by the fact that in this region of decomposition, poly(methyl acrylate) decomposes completely, thus lowering the temperature of decomposition of the grafted sample.

Cellulose grafted with ethyl acrylate behaves exactly in a similar way as cellulose grafted with methyl acrylate as shown in Figure 5. The T_D values at different weight losses for cotton grafted with 10%, 55%, and 91% ethyl acrylate are given in Table III. In this case also the decomposition is greatly influenced by the per cent graft-on, and at any particular temperature, weight loss is more in the case of natural cotton than for the samples
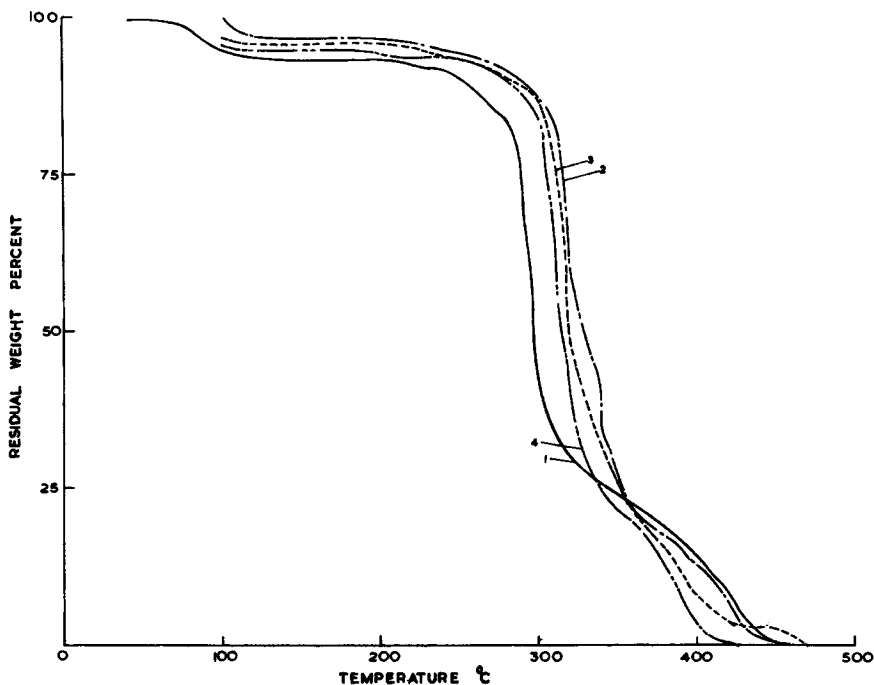
Fig. 5. Primary thermograms of natural cotton and cotton grafted with ethyl acrylate: (1) natural cotton; (2) 10% graft copolymerized; (3) 55% graft copolymerized; (4) 91% graft copolymerized.

grafted with ethyl acrylate; and this is more predominant in the case of samples with higher percentage graft-on up to 350°C.

The effect of grafting n-butyl acrylate onto cellulose is to lower the thermal stability of the grafted samples, as is evident from Figure 6 and T_D values at different per cent weight losses given in Table III.

Primary thermograms of methyl methacrylate-grafted cellulose up to 40% graft-on indicate a decrease in thermal stability in comparison to natural cellulose. But at 55% graft-on, the thermal stability of grafted cotton is almost equal to that of natural cellulose (Fig. 7). The T_D values at different percentage weight losses are given in Table III.

Initial decomposition temperatures (IDT) of natural cellulose and cellulose grafted with acrylate monomers are given in Table IV. The value of IDT of natural cellulose is 210°C, whereas those of 15%, 62%, and 74% methyl acrylate-grafted cottons are 220°C, 240°C, and 240°C, respectively. Similar increases in IDT with increase in per cent graft-on are observed in the other cases also.

The integral procedural decomposition temperature (IPDT) as proposed by Doyle[11] to find out the integral end of the volatilization temperature was calculated for the different grafted samples and for the natural cotton. The results are presented in Table IV. The IPDT values increase with
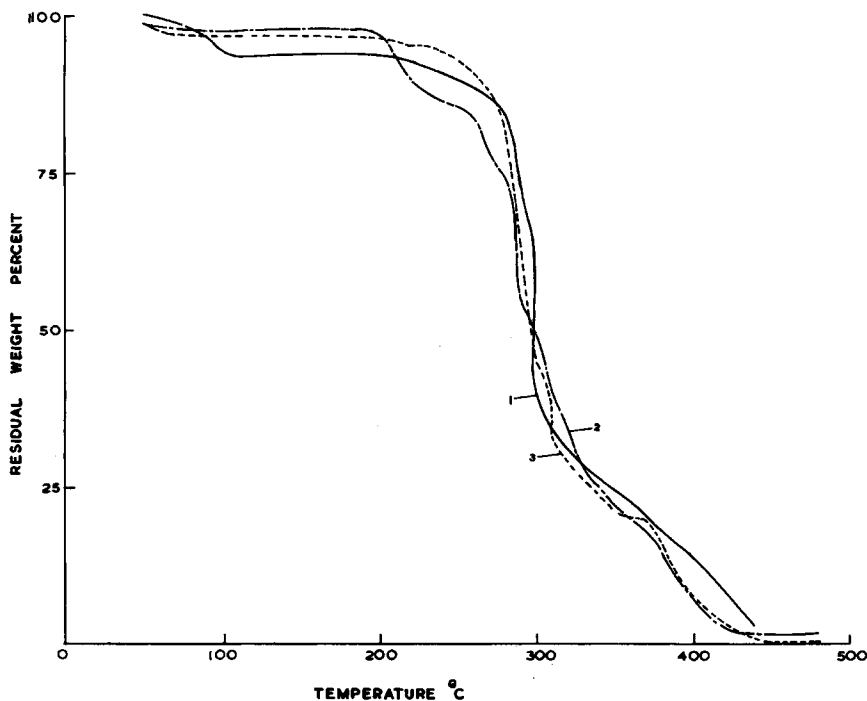
Fig. 6. Primary thermograms of natural cotton and cotton grafted with n-butyl acrylate: (1) natural cotton; (2) 20.5% graft copolymerized; (3) 72% graft copolymerized.

increase in graft-on per cent. The *IPDT* values of cotton grafted with methyl acrylate and ethyl acrylate are higher than that of natural cotton, whereas those of cotton grafted with n-butyl acrylate and methyl methacrylate are lower.

To understand the energetics of the reaction, the activation energy E^* for the decomposition reaction in the temperature range of 270°C–340°C was calculated. It has been earlier reported that in this temperature range the thermal degradation of cellulosic materials follow a pseudofirst-order reaction.[16] Activation energy was calculated using the method given by Dharwadkar and Karkhanawala.[17] According to their equation

$$\ln \ln(1 - \alpha)^{-1} = \frac{E^*}{RT_i{}^2} \frac{100}{T_f - T_i} \theta + C$$

where α = fraction reacted, E^* = activation energy, T_i = temperature of inception of reaction, T_f = temperature of completion of the reaction, T_s = temperature at the point of inflection on the thermogram, θ = difference between T_s and the temperature under consideration $(T - T_s)$, C = constant, and R = gas constant.

This equation is independent of sample size and heating rate, while the equations proposed by Freeman-Carroll,[18] Horowitz and Metzger,[19] and

TABLE III
Decomposition Temperatures T_D at Different Weight Losses

| Sample	Graft-on, %	T_D, °C, at per cent weight loss of								
		10%	20%	30%	40%	50%	60%	70%	80%	90%
Natural cotton	0	274	290	294	294	296	300	330	378	414
Methyl acrylate-grafted cotton	15	282	296	300	300	302	306	322	360	402
	62	298	306	312	318	326	336	342	362	400
	74	296	304	310	310	320	338	346	362	402
Ethyl acrylate-grafted cotton	10	298	306	312	316	320	325	332	362	390
	55	296	302	310	320	322	333	346	368	412
	91	294	300	318	324	333	342	350	368	396
Butyl acrylate-grafted cotton	20.5	274	288	292	292	298	304	320	366	394
	72	230	272	286	290	302	314	332	360	392
Methyl methacrylate-grafted cotton	13.5	274	280	283	284	288	295	302	328	382
	38	278	286	290	290	290	298	304	324	372
	55	281	290	292	293	277	304	312	318	370
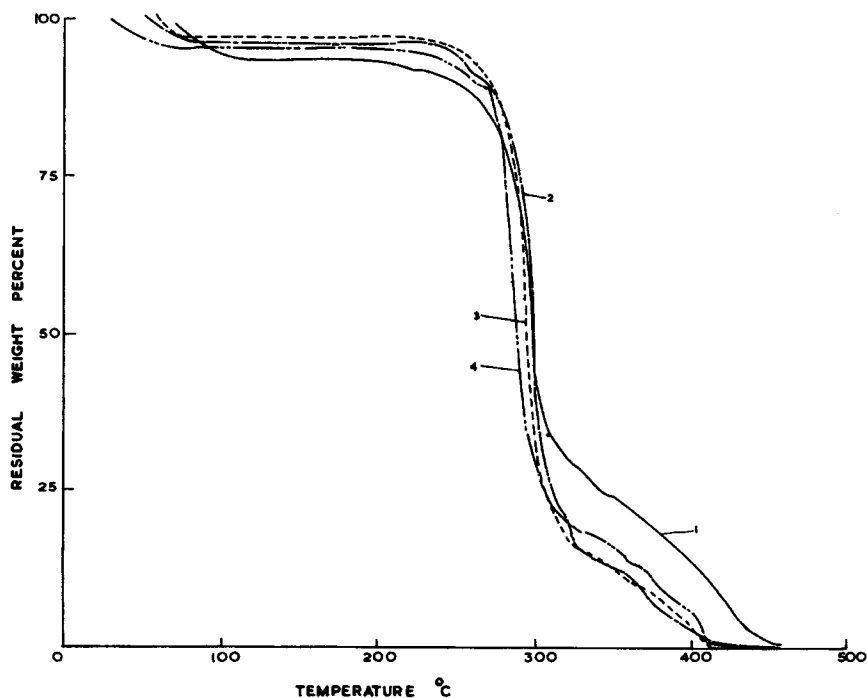
Fig. 7. Primary thermograms of natural cotton and cotton grafted with methyl methacrylate: (1) natural cotton; (2) 13.5% graft copolymerized; (3) 38% graft copoly-merized; (4) 55% graft copolymerized.

TABLE IV
Thermogravimetric Analysis of Copolymerized and Natural Cotton

| Sample	Per cent copoly-merized, %	Initial de-composition temp. (IDT), °C	IPDT, °C	Activation energy E^*, kcal/mole
Natural cotton	0	210	322	32
Methyl acrylate-grafted cotton	15	220	324	32
	62	240	334	34
	74	240	335	36
Ethyl acrylate-grafted cotton	10	210	326	36
	55	220	337	34
	91	220	338	36
Butyl acrylate-grafted cotton	20.5	210	322	23
	72	210	312	21
Methyl methacrylate-grafted cotton	13.5	230	306	30
	38	240	308	31
	55	240	312	31
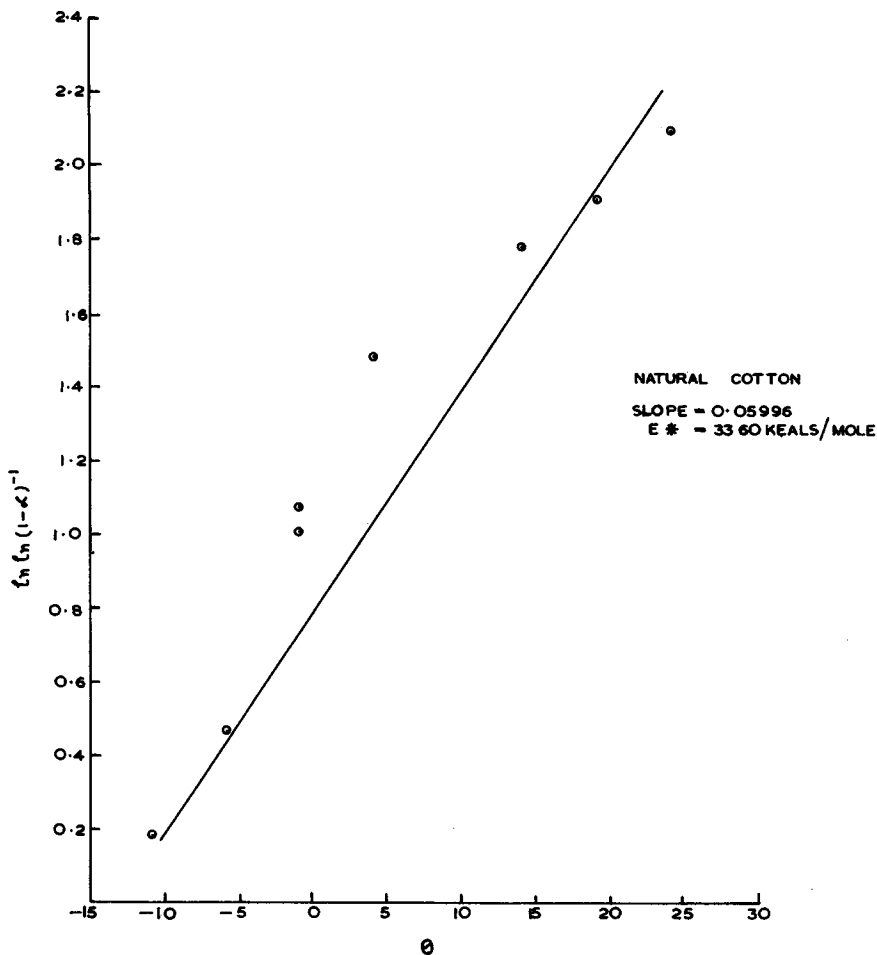
Fig. 8. A plot of $\ln \ln(1 - \alpha)^{-1}$ vs. θ for natural cotton.

Coats and Redfern[20] do not take into account the variations obtained in the value of energy of activation due to variations in the sample size and heating rate. To calculate the value of E^* accurately and in a reproducible manner, the primary thermograms of the dried samples were drawn on an expanded scale; T_i was measured accurately as the temperature at which the decomposition starts, and T_f was taken as the temperature at which the main decomposition is complete. In all the samples, a similar procedure for the evaluation of activation energy was used. The values of E^* thus obtained may not represent the absolute value of activation energy, but we were interested in relative values of E^* for the grafted cotton samples.

Values of $\ln \ln (1 - \alpha)^{-1}$ were plotted versus the corresponding θ values, and a straight line was obtained. The slope of the straight line is $(E^*/RT_i^2)(100/T_f - T_i)$, from which the activation energy can be calculated. A typical plot of $\ln \ln(1 - \alpha)^{-1}$ versus θ is given for natural cotton in

Figure 8. In view of the small scatter of the points about the straight line, a least-squares slope was calculated to evaluate the activation energy. The values of activation energy for the decomposition of the samples of cellulose and cellulose grafted with different monomers to various extents of grafting are shown in Table IV. The activation energies of decomposition of cellulose grafted with methyl acrylate and ethyl acrylate are higher than that of natural cotton; those of cellulose grafted with n-butyl acrylate and methyl methacrylate are lower than that of natural cotton. It can also be observed from Table IV that the activation energy increases with increasing per cent graft-on in all the cases except for cellulose grafted with n-butyl acrylate.

Since the main decomposition of all these samples takes place in the temperature range of 240°C to 340°C, we can construe that the magnitude of the energy of activation is a measure of the thermal stability of the samples. The results in Table IV lead us to the conclusion that the thermal stability of the grafted samples increases with the per cent graft-on in all the cases; the thermal stabilities for cellulose grafted with different monomers can be written in the form ethyl > methyl > natural cellulose > methyl methacrylate > n-butyl acrylate. Contrary to the results obtained by Hurduc et al.[10] who have pointed out that the thermal stability of natural cellulose is greater than that of grafted cellulose, we have found that the thermal stability of cellulose grafted with methyl and ethyl acrylates is higher than that of natural cellulose, as is evident from the IDT, $IPDT$, and E^* values.

References

1. S. Kaizerman, G. Mino, and L. F. Meinhold, *Text. Res. J.*, **32**, 136 (1962).
2. M. Negishi, Y. Nakamura, T. Kakinuma, and Y. Iizuka, *J. Appl. Polym. Sci.*, **9**, 2227 (1965).
3. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1625 (1968).
4. M. V. Ramaiah, *J. Appl. Polym. Sci.*, **14**, 1323 (1970).
5. N. Hurduc, I. A. Schneider, and CR. Simionescu, *Cell. Chem. Technol.*, **2**, 569 (1968).
6. P. K. Chatterjee and C. M. Conrad, *Text. Res. J.*, **36**, 487 (1966).
7. C. M. Conrad and D. J. Stanonis, *Appl. Polym. Symposia*, **No. 2**, 121 (1966).
8. L. E. A. Godfrey, *Text. Res. J.*, **40** 116 (1970).
9. S. R. Hobart, R. J. Berni, and C. H. Mack, *Text. Res. J.*, **40**, 1079 (1970).
10. N. Hurduc, CR. Simionescu, and I. A. Schneider, *Cell. Chem. Technol.*, **5**, 37 (1971).
11. C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
12. S. Ranga Rao and S. L. Kapur, *J. Appl. Polym. Sci.*, **13**, 2649 (1969).
13. Y. Ogiwara, Y. Ogiwara, and H. Kubota, *J. Polym. Sci. A-1*, **5**, 2791 (1967).
14. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference, J. Polym. Sci, C*, **2**, 403 (1963), R. H. Murchessault, Ed., Interscience, New York, 1963, p. 523.

15. R. F. Schwenker, Jr., L. R. Beck, Jr., and R. K. Zuccarello, *Amer. Dyestuff Rep.*, **53,** 817 (1964).

16. P. K. Chatterjee and C. M. Conrad, *J. Polym. Sci. A-1*, **6,** 3217 (1968).

17. S. R. Dharwadkar and M. D. Karkhanawala, "Thermal Analysis" in *Inorganic Materials and Physical Chemistry*, Vol. 2, R. F. Shwenker and P. D. Garn, Eds., Academic Press, New York/London, 1969.

18. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62,** 394 (1958).

19. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35,** 1464 (1963).

20. A. W. Coats and J. R. Redfern, *Nature*, **201,** 68 (1964).