Radiation-Induced Graft Copolymerization of Mixtures of Styrene and Acrylamide onto Cellulose Acetate. V. Studies on Thermal Behavior

S. N. BHATTACHARYYA and D. MALDAS, *Nuclear Chemistry Division, Saha Institute of Nuclear Physics, 92, Acharya Prafulla Chandra Road, Calcutta 700009, India*

Synopsis

The thermal behaviors of cellulose acetate, either grafted or ungrafted, were studied. A thermogram of cellulose acetate when grafted with acrylamide is characterized by an endothermic peak at 340°C. If, however, styrene is grafted, the thermogram shows two characteristic exothermic peaks at 330 and 420°C. A thermogram of the mixed graft comprising both acrylamide and styrene, on the other hand, is characterized by only one exothermic peak at 420°C. A consideration of various thermal data indicates that cellulose acetate when grafted is comparatively more stable than when not grafted. Again, styrene is found to be more effective than acrylamide in increasing the stability.

INTRODUCTION

The thermal behavior of modified cellulosics is of great importance.[1-3] A limited number of reports are only available in connection with the thermal behavior of cellulose when grafted with a single monomer.[4-9] If, however, two monomers, e.g., styrene and acrylamide are involved, as in the present investigation, the thermal behavior of such a binary system is, of course, scarcely studied.[10]

EXPERIMENTAL

The detailed procedure for the preparation of cellulose acetate film as well as graft copolymerization from binary monomer systems of styrene and acrylamide have been reported earlier.[11]

The thermogravimetric analyses of ungrafted cellulose acetate, acrylamide-grafted, styrene-grafted, and mixed monomer-grafted cellulose acetate were carried out using a Derivatograph (Hungary). The analyses were done in air from room temperature to 600°C at a heating rate of 8°C/min.

RESULTS AND DISCUSSION

Figure 1 shows the thermogram of ungrafted cellulose acetate. The thermal behaviors of cellulose acetate when grafted with acrylamide, styrene, or with a mixture of the two are shown, respectively, in Figures 2–4. The differential thermal analysis (DTA) curves indicate that the first decom-

Journal of Applied Polymer Science, Vol. 30, 151–158 (1985)
 CCC 0021-8995/85/010151-08$04.00

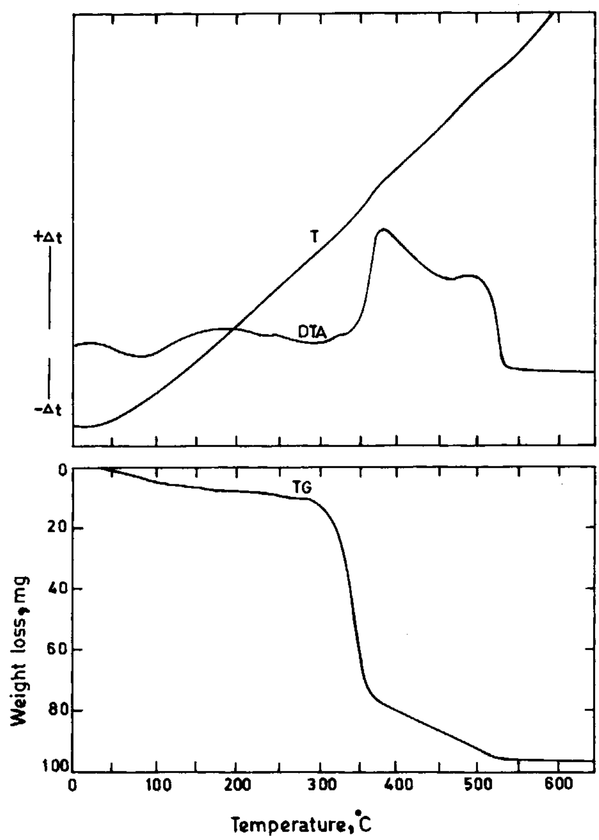

Fig. 1. Thermogram of ungrafted cellulose acetate.

position stage occurs at about 150°C, which is further confirmed by the thermogram (TG) curves, where some loss in weight is observed. This weight loss is not appreciable and this may arise[12] from the loss of adsorbed water. Attention should, however, be drawn to the fact that this weight loss is characteristic of both grafted and ungrafted films. The subsequent stages of decomposition are, however, different in case the trunk polymer is grafted or not and, moreover, the point of decomposition is also dependent on the nature of grafting. If the curve indicating the DTA of acrylamide-grafted cellulose acetate is compared with that of the ungrafted film, the former is only found to be characterized by an endothermic peak[10,13] at ca. 340°C. Similarly, the DTA curve of styrene-grafted copolymer is found to be characterized[13] by two exothermic peaks at 330 and 420°C. When both styrene and acrylamide are grafted, the DTA of the mixed graft is found to be characterized by only an exothermic peak at 420°C like the styrene-grafted copolymer, whereas the endothermic peak due to acrylamide and the exothermic peak due to styrene at lower temperatures appear to converge leading particularly to no characteristic decomposition pattern at lower temperature.

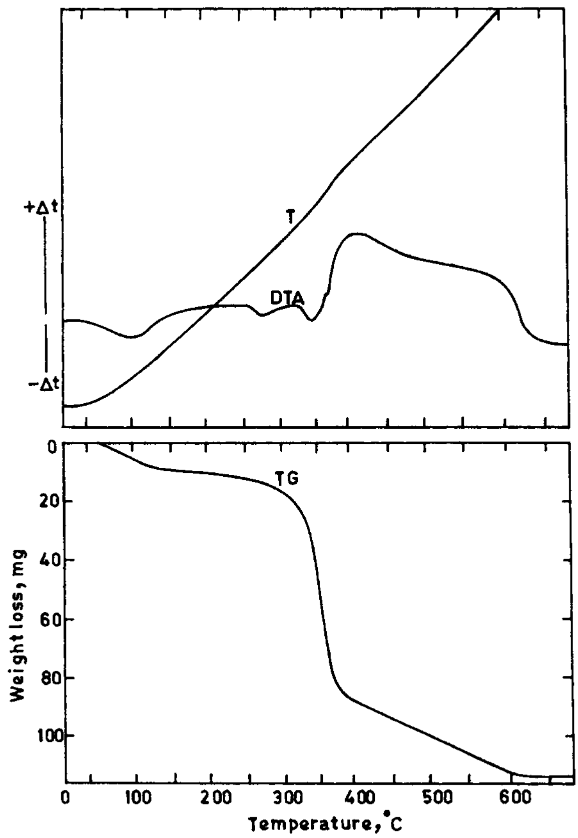

Fig. 2. Thermogram of acrylamide-grafted (11.1%) cellulose acetate.

A comparison of the area of the peak observed at 420°C for the mixed graft with that observed when styrene alone is grafted yields interesting findings. The results are shown in Table I.

It is evident from Table I that when styrene is grafted singly, exothermicity increases with the increase in the extent of styrene grafted. If grafting is carried out from its binary mixture with acrylamide, incorporation of even 4% acrylamide in the mixed graft has a tendency to decrease the total heat change. This is true if the percentage of styrene in the mixed graft is reasonably low, e.g., ca. 7%. If, however, the percentage of styrene is increased considerably, say, 18%, the exothermicity tends to increase significantly, e.g., three to four times that which is observed when styrene is grafted alone. Hence, it may be inferred that the higher the percentage of styrene grafted, the higher the heat change in the mixed graft.

The TG curves of the ungrafted cellulose acetate and various grafted cellulose acetate are very similar. To understand the thermal stability of grafted cellulose acetate compared with that of ungrafted ones, the decomposition temperature (T_D) at various weight losses was determined and listed in Table II.

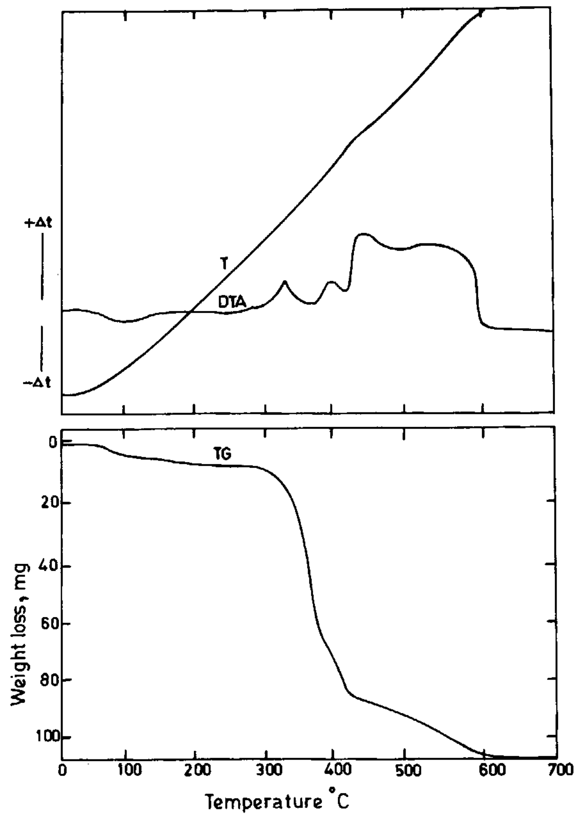

Fig. 3. Thermogram of styrene-grafted (22.3%) cellulose acetate.

From Table II it is evident that the decomposition temperature, in general, increases with grafting, be it grafting with acrylamide or with styrene. T_D values are larger when cellulose acetate is grafted with styrene than when grafted with acrylamide. In the mixed graft, again, incorporation of acrylamide has a tendency to lower the T_D values, and with the increase in the extent of grafting of styrene T_D values tend to increase. The aforesaid picture is true if the weight loss is larger, say, 30% and onward. If, however, a weight loss of ca. 10% is considered, the T_D values in the mixed graft not only increase with the increase in the extent of grafting of styrene, but even surpass the value for pure styrene grafting under conditions such that the composition of styrene and acrylamide in the mixed graft is ca. 6:1. Thus, at lower weight loss the effect of one on the other in the mixed graft is not simply additive in affecting the decomposition temperature. It is, however, interesting to note that when styrene is grafted in larger proportion than that of acrylamide, the T_D values are such that it can be inferred that the mixed grafts under such condition are more stable than when styrene is grafted alone.

Furthermore, from the thermograms the temperature range at which the main decomposition occurs, was determined and listed in Table III. For

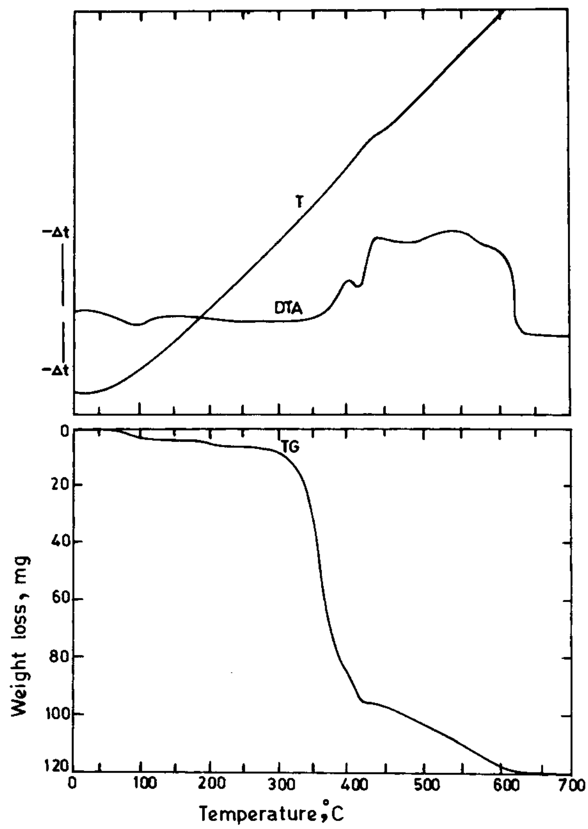

Fig. 4. Thermogram of cellulose acetate grafted with a mixture of acrylamide and styrene (total grafting = 22.5%; acrylamide = 4.1%, and styrene = 18.4%).

ungrafted cellulose acetate the initial decomposition temperature (IDT) is 290°C and the final decomposition temperature (FDT) is 390°C. When individual monomers are grafted onto cellulose acetate, IDT is somewhat similar to that of ungrafted cellulose acetate. When two monomers are grafted onto cellulose acetate, the IDT is slightly higher than in the case of ungrafted cellulose acetate or when only one monomer is grafted on cellulose acetate. When acrylamide is grafted, FDT increases with the increase in the extent of graft copolymerization, so also is the behavior when grafting styrene alone. The case of mixed graft increasing the incorporation of styrene was found to lead to an increase of FDT, which, in other words, indicates an increased stability for such a mixed graft.

Similar conclusions can also be arrived at from a consideration of integral procedual decomposition temperature[14] (IDPT). Here, again, it is observed (Table III) that the role of styrene consists of increasing the IPDT values in the mixed graft as observed in the case of grafting of the styrene alone.

The activation energies for the main decomposition of ungrafted and grafted cellulose acetate were determined according to the method given by Dharwadkar and Karkhanawala.[15]

TABLE I
Peak Areas of Thermograms at 420°C

Grafting condition	Composition of the graft: Styrene (%)	Acrylamide (%)	Total (%)	Peak area (cm^2/mg)
Only styrene is grafted	11.2	—	11.2	4.3×10^{-3}
	22.3	—	22.3	4.5×10^{-3}
Mixed graft	7.4	4.0	11.4	4.2×10^{-3}
	18.4	4.1	22.5	14.8×10^{-3}

TABLE II
Decomposition Temperatures (T_D) at Different Weight Losses of Ungrafted and Grafted Cellulose Acetate

Grafting condition	% Grafting	Temperature of decomposition in °C at weight loss of: 10%	20%	30%	40%	50%	60%	70%	80%	90%
Ungrafted		268	317	330	335	340	347	354	388	455
Acrylamide	11.1	280	322	338	345	350	360	368	410	495
grafted	33.9	280	325	345	350	355	365	375	415	495
Styrene	11.2	301	335	348	355	365	370	390	415	525
grafted	22.3	302	335	352	360	368	375	395	425	525
	Acrylamide: Styrene ratio in the graft copolymer									
1:1.8	11.4	285	320	332	337	345	350	355	390	500
1:4.5	22.5	310	335	350	358	368	375	390	420	515
1:5.9	33.4	310	337	350	358	368	380	390	420	515

TABLE III
Thermogravimetric Analysis of Ungrafted and Grafted Cellulose Acetate

Grafting condition	% Grafting	IDT[a]	FDT[b]	IPDT[c]	E^* (kcal/mol)
Ungrafted		290	390	338.8	21.6
Acrylamide	11.1	290	410	336.7	25.2
grafted	33.9	290	440	365.6	27.7
Styrene	11.2	280	440	359.3	31.1
grafted	22.3	290	440	376.5	33.1
	Acrylamide: Styrene ratio in the graft copolymer				
1:1.8	11.4	300	415	358.1	28.2
1:4.5	22.5	300	435	361.6	29.1
1:5.9	33.4	305	430	364.1	29.9

[a] Initial decomposition temperature.
[b] Final decomposition temperature.
[c] Integral procedual decomposition temperature.

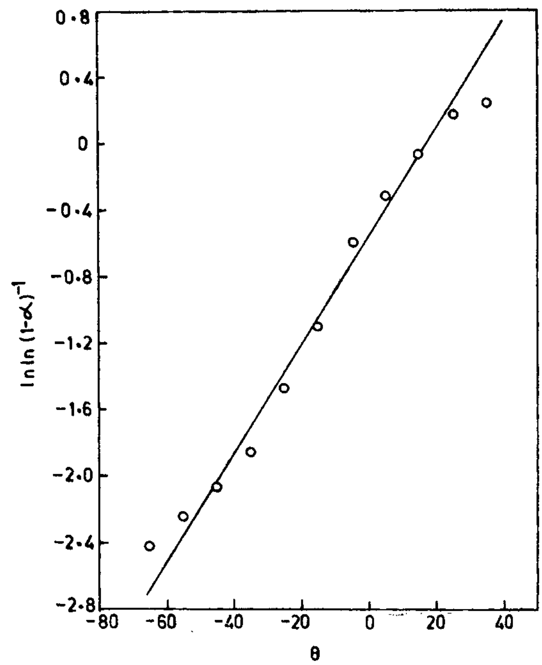

Fig. 5. A typical plot of ln ln(1 − α)$^{-1}$ vs. Θ, where acrylamide is grafted to cellulose acetate (extent of grafting = 11.1%).

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

where α is fraction reacted, E^* is the activation energy, Θ is the temperature under consideration—inflection temperature, R is the gas constant, T_i is the temperature of inception of reaction, T_f is the temperature of completion of the reaction, and C is a constant. A plot of ln ln(1 − α)$^{-1}$ against Θ should yield a straight line. A typical plot is shown in Figure 5. From the slopes of such straight lines the activation energies of the main decomposition were therefore calculated. The observed E^* values are given in Table III. A consideration of these E^* values again leads to the same conclusion as discussed above. What transpires, in general, from the observed results is that cellulose acetate when grafted is more stable than when it is not grated. Moreover, styrene has a more positive effect than acrylamide in increasing the stability of the graft.

We are thankful to Dr. N. K. Roychowdhury of the Indian Association for the Cultivation of Sciences, Calcutta, for using the Derivatograph.

References

1. H. Anderson, Jr., E. Bartkus, and J. Reynolds, *IBM J. Res. Dev.*, **140**, March (1971).
2. C. I. Simionescu, F. Dénes, M. M. Macoveanu, G. Cazacu, M. Totolin, S. Percec, and D. Balaur, *Cellul. Chem. Technol.*, **14**, 869 (1980).
3. A. Mey-Marom and D. Behar, *J. Appl. Polym. Sci.*, **25**, 691 (1980).

4. Z. A. Rogovin, *J. Polym. Sci., C,* **37**, 221 (1972).
5. N. Hurduc, C. I. Simionescu, and I. A. Schneider, *Cellul. Chem. Technol.,* **5**, 37 (1971).
6. C. I. Simionescu, I. A. Schneider, and N. Hurduc, *J. Polym. Sci., Polym. Chem. Ed.,* **10**, 325 (1972).
7. D. S. Varma and V. Narasimhan, *J. Appl. Polym. Sci.,* **16**, 3325 (1972).
8. G. Odian and J. Tsay, *Makromol. Chem.,* **182**, 1481 (1981).
9. Yu. N. Sazanov, G. N. Fedorova, A. A. Berlin, and V. N. Kisilenko, *Cellul. Chem. Technol.,* **15**, 205 (1981).
10. V. N. Sharma and E. H. Daruwala, *J. Appl. Polym. Sci.,* **21**, 331 (1977).
11. S. N. Bhattacharyya and D. Maldas, *J. Polym. Sci., Polym. Chem. Ed.,* **20**, 939 (1982).
12. R. F. Schwenker, Jr., L. R. Beck, Jr., and R. K. Zuccarello, *Am. Dyestuff Rep.,* **53**, 817 (1964).
13. R. T. Conley, *Thermal Stability of Polymers,* Dekker, New York, 1970, Vol. 1.
14. C. D. Doyle, *Anal. Chem.,* **33**, 77 (1961).
15. S. R. Dharwadkar and M. D. Karkhanawala, "Thermal Analysis," in *Inorganic Materials and Physical Chemistry,* R. F. Schwenker and P. D. Garn, Eds., Academic, New York, 1969, Vol. 2.

Received October 27, 1983
Accepted March 16, 1984
Corrected proofs received November 26, 1984