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Grafting Vinyl Monomers onto Nylon 6 Fiber. II. Graft Copolymerization of Methyl Methacrylate onto Nylon 6 Fiber by Photoirradiation in the Presence of Fructose

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ABSTRACT

Photopolymerization of methyl methacrylate (MMA) onto nylon 6 fiber by UV radiation in alcoholic solutions of water-methanol, water-ethanol, and water-n-propanol in the presence of fructose was investigated. The effects of monomer concentration, time of polymerization, fructose concentration, and effect of media have also been studied. Graft add-on (GAO) % greatly enhanced with an increase in monomer concentration and time. With fructose concentration it increases up to 15 mmol/L of fructose and thereafter falls. The GAO in the media is in the following order: $W + M + F > W + E + F > W + P + F$ (W = water; M = methanol; E = ethanol; P = n-propanol). A probable mechanism has been suggested. It appears that the active site is formed on MMA which abstracts an H-atom from the nylon 6 backbone, giving rise to graft of MMA by mutual combination.

EXPERIMENTAL

Nylon 6 fiber, methanol, ethanol, n-propanol, and MMA are the same as mentioned in our previous paper [1]. Acetone supplied by BDH Laboratories and fructose of AR grade, also supplied by BDH Laboratories, have been used. Acetone was distilled prior to use whereas fructose was used as received. Double distilled water was used. The grafting technique using a photoirradiation source was the same as used previously [1].

RESULTS AND DISCUSSION

Grafting of nylon 6 fiber was carried out using MMA as monomer in the presence of a carbon arc lamp as the source of photochemical initiation in the presence of water-methanol, water-ethanol, and water-n-propanol as the reaction media (water-alcohol ratio 1:1) at 70°C. To find the effect of fructose on MMA polymerization, another polymerization experiment under similar conditions, i.e., liquid ratio 1:26, temperature 70°C, time of polymerization 90 min, and fructose concentration 10 mmol/L in the presence of UV light, was carried out, giving a yield of 44.3%. Similar results have been obtained by Kubota and Ogiwara [2]. However, it was also noted that no grafting takes place under similar conditions when the media is either water alone or pure alcohol. In the present paper the effects of various parameters (monomer concentration, time, fructose concentration, medium) on grafting have been investigated.

EFFECT OF MONOMER CONCENTRATION
ON GRAFTINGWater-Methanol 1:1 Ratio

Nylon 6 fiber was grafted using a fructose concentration of 10 mmol/L, liquor ratio 1:26 (1 mL of MMA and 25 mL of water-alcohol), 70°C, for 90 min, using a carbon arc lamp at four different monomer concentrations. The results are presented in Fig. 1.

From the results it can be seen that the % GAO goes up continuously. The grafting efficiency increases, reaches a maximum, and then falls. Several other workers [3-5] have found similar results on GAO with an increase of monomer concentration.

Water-Ethanol 1:1 Ratio

The conditions of grafting are the same as used in the above case. The results are presented in Fig. 2. From the results it can be seen

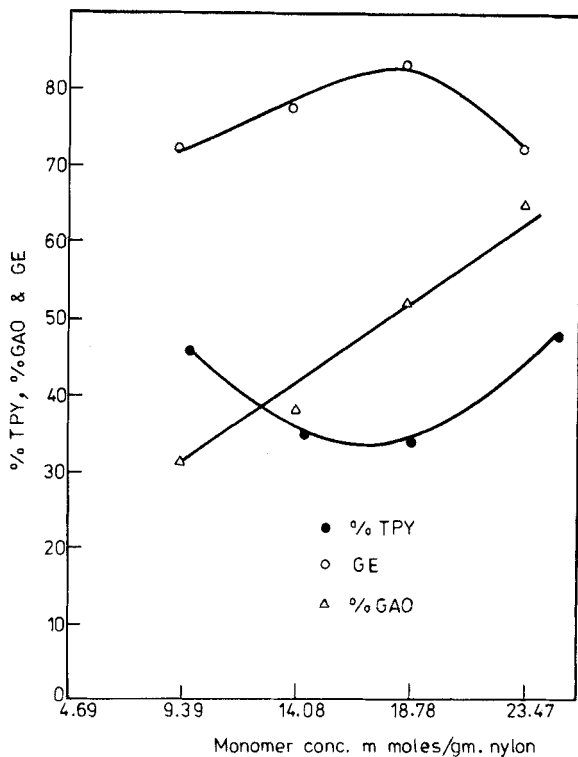


FIG. 1. Effect of monomer concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-methanol 1:1), 1:26; time, 90 min, temperature 70°C; fructose concentration, 10 mmol/L. (●) % Total polymer yield (TPY), (△) % graft add-on (GAO), (○) grafting efficiency (GE).

that the % conversion increases continuously with an increase in monomer concentration. Grafting efficiency (GE) also increases at first and then falls. Percent homopolymer yield formation decreases, however, and as a consequence the grafting efficiency increases.

Water-n-Propanol 1:1

In this case the reaction conditions are also the same as used in the above two cases. The results are presented in Fig. 3. Here the GAO increases as the monomer concentration increases. The grafting efficiency also increases as noted in the above two cases.

From the results in the three different media, it is seen that with

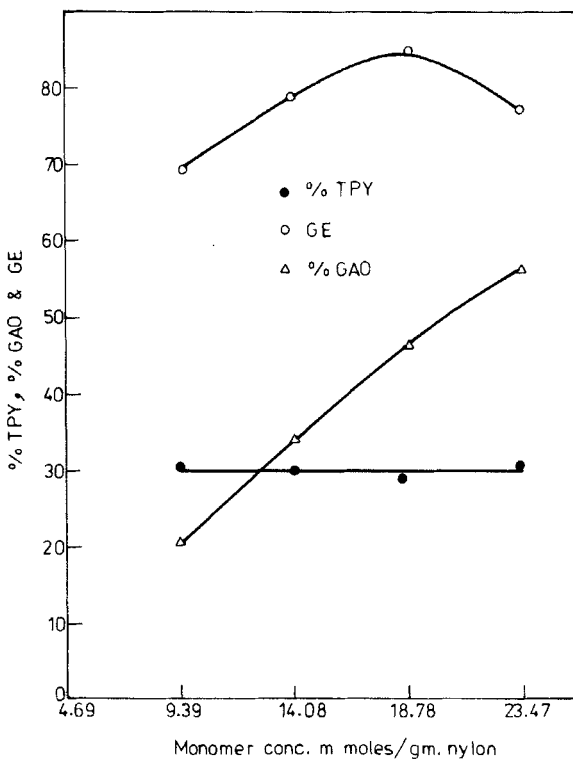


FIG. 2. Effect of monomer concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-ethanol 1:1), 1:26; time, 90 min; temperature 70°C; fructose concentration, 10 mmol/L.

increase in monomer concentration there is an increase in % TPY and % GAO. However, polymerization is most favored in the water-methanol medium, followed by water-ethanol and water-n-propanol media in that order. This trend is similar to that observed in the study without the presence of fructose [1]. This trend follows the trend of solubility of the monomer in these media as well as the dielectric constant values of the alcohols, i.e., methanol > ethanol > n-propanol.

There is a constant increase in GE with an increase in MMA concentration in all cases to a maximum and then it falls. This shows that in the initial stages the grafting reaction is favored more than the homopolymer reaction. Similar results have been found by several workers [3-5] with an increase in monomer concentration. The subsequent decrease may be attributed to the gel effect due to high monomer concentration. An interesting point to note is that a MMA

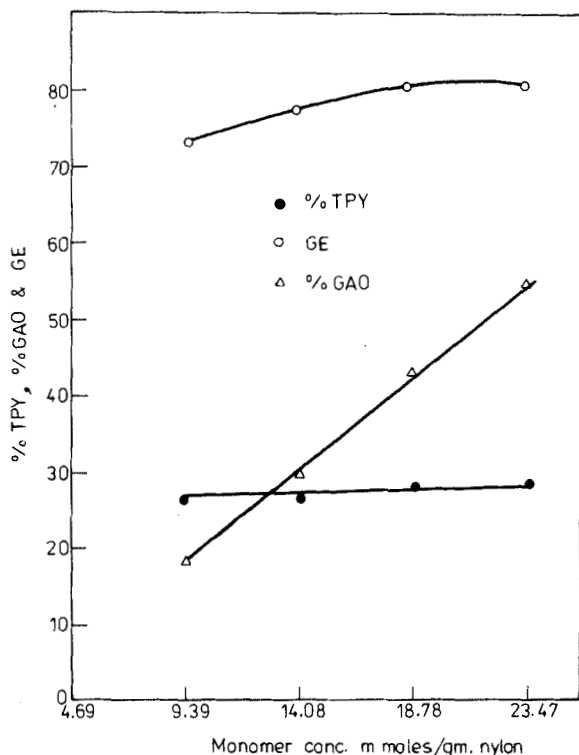


FIG. 3. Effect of monomer concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-propanol 1:1), 1:26; time, 90 min; temperature 70°C; fructose concentration, 10 mmol/L.

concentration of 18.78 mmol/g nylon seems to be the optimum concentration in all the three media as far as the GE is concerned.

EFFECT OF THE TIME ON GRAFTING

Water-Methanol 1:1 Ratio

Nylon 6 fiber was grafted with MMA using 1 g of the fiber at 70°C, a liquor ratio of 1:26, and a fructose concentration of 10 mmol/L. The temperature was varied from 60 to 150 min. The results are presented in Fig. 4. The GAO increases continuously as does the total conversion percentage. However, the GE increases to a

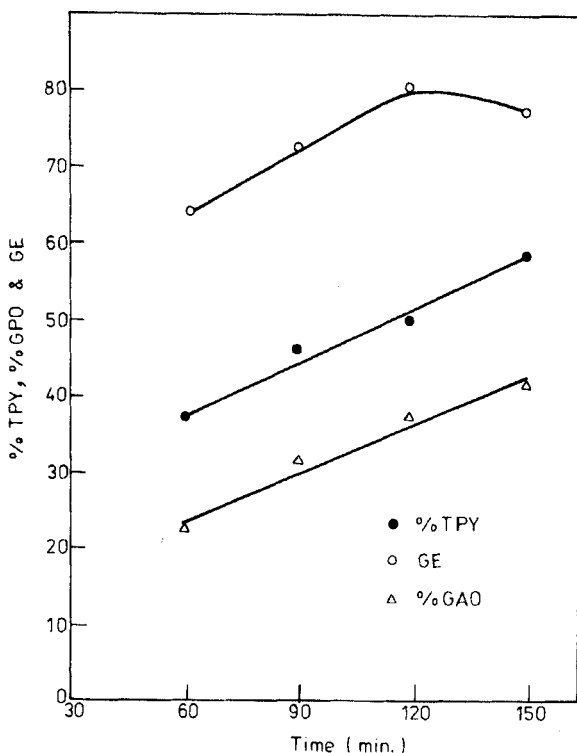


FIG. 4. Effect of reaction time on grafting. Nylon 6 fiber, 1 g, monomer concentration, 9.39 mmol/g nylon; temperature, 70°C; liquor ratio (water-methanol 1:1), 1:26; fructose concentration, 10 mmol/L.

maximum and then falls. Because a large amount of grafting has taken place, further polymerization and hence % TPY does not increase. A chain transfer reaction involving homopolymerization on one hand and nylon fiber on the other can take place. If this happens, the % HPY decreases and as a consequence GE increases. Chain transfer reactions involving polymers are well known, and MMA is no exception [6].

Water-Ethanol 1:1 Ratio

Nylon 6 fiber was grafted with MMA using 1 g nylon fiber, a monomer concentration of 9.39 mmol/g, and a nylon liquid ratio of 1:26 at 70°C. The results are presented in Fig. 5.

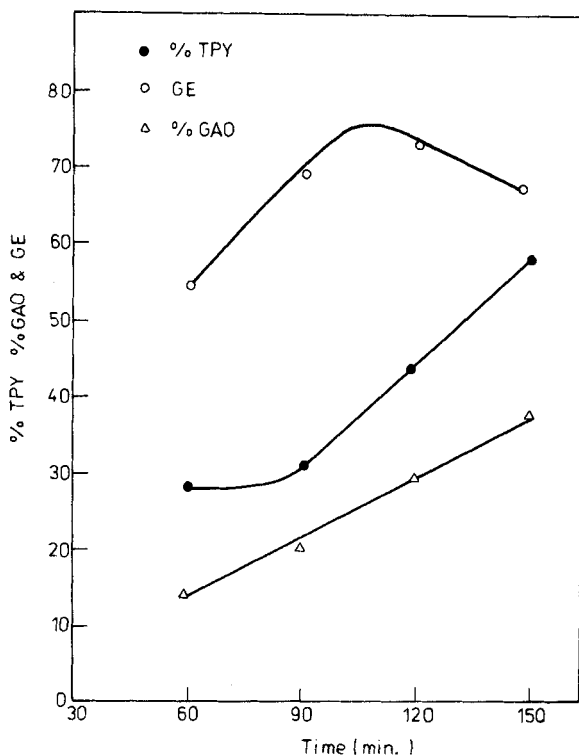


FIG. 5. Effect of reaction time on grafting. Nylon 6 fiber, 1 g; monomer concentration, 9.39 mmol/g nylon; temperature, 70°C, liquor ratio (water-ethanol 1:1), 1:26; fructose concentration, 10 mmol/L.

From the results it is seen that the % GAO and % TPY increases as in the above case. The GE also behaves in a similar fashion. All these results are similar to what was observed in the water-methanol system except that the % conversion decreases in the water-ethanol system as compared to the water-methanol system. This seems to be due to effect of the media. Similar results for the effect of media were also obtained by Nayak and co-workers while grafting vinyl monomers onto wool fibers [8].

Water-n-Propanol 1:1 Ratio

Nylon 6 fiber was grafted with MMA taking 1 g of the fiber and a liquid 1:26 ratio at 70°C with a monomer concentration 9.39 mmol/g nylon. The results are presented in Fig. 6.

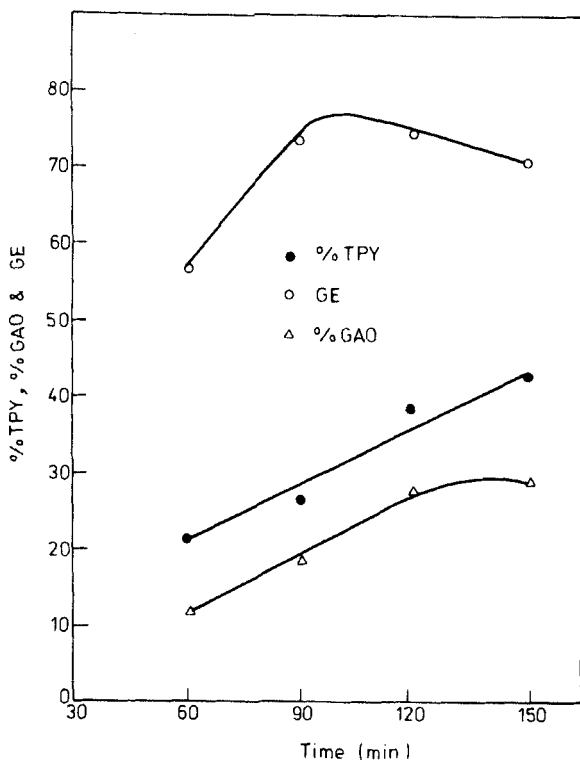


FIG. 6. Effect of reaction time on grafting. Nylon 6 fiber, 1 g; monomer concentration, 9.39 mmol/g nylon; temperature, 70°C, liquor ratio (water-propano 1:1), 1:26; fructose concentration, 10 mmol/L.

These results show that the reaction behavior in this case is similar to those observed in the above two cases, but the % conversion is lower. Reactions involving chain transfer seem to be applicable here, and the solubility factor comes into play once again as regards the low percentage conversion. The solubility behavior of MMA in all the above solvents has been explained in our previous paper [1].

With an increase in the time period, both % TPY and % GAO show a continuous and linear increase. The values of the slopes of the curves of % GAO vs time in minutes are given in Figs. 4, 5, and 6 for the three different media in Table 1.

Hence the TPY and GAO increase at the fastest rate in the water-ethanol system. However, as regards GAO and TPY under similar

TABLE 1

Medium	Value of the slope for	
	TPY \times 10	GAO \times 10
1. Water-methanol 1:1	2.25	2.00
2. Water-ethanol 1:1	4.50	2.50
3. Water-n-propanol 1:1	2.30	2.16

conditions, the water-methanol system gives the maximum values. The GE, on the other hand, is a maximum in the case of the water-methanol system followed by the water-n-propanol and then by the water-ethanol system.

EFFECT OF FRUCTOSE CONCENTRATION ON GRAFTING

Nylon 6 was grafted with MMA using 1 g nylon 6 fiber and 9.39 mmol/g nylon of the monomer at 70°C for 90 min. The concentration of fructose has been changed fourfold. Grafting does take place in the absence of fructose, contrary to what was observed in water media alone where no grafting occurred under similar conditions. However, as the fructose concentration in water-methanol, water-ethanol, and water-n-propanol increases, the % GAO, % TPY, and GE all show an increasing trend.

An ESR study [2] of the photopolymerization of the MMA-fructose-MeOH system in hard glass did not show any radicals formation on fructose, thus no photodecomposition of fructose takes place. No change in the reducing power of fructose was observed in the same study. Hence the acceleration of photopolymerization of MMA in that system by fructose was attributed to the sensitizing action of fructose involving an energy transfer. It does not undergo initiation at the glucosidic bond.

The results of the effect of fructose concentration on grafting in water-methanol, water-ethanol, and water-n-propanol media are presented in Figs. 7, 8, and 9, respectively. The trend for % TPY, % GAP, and GE is similar in all these cases. The % TPY, % GAO, and GE increase until a concentration of fructose of the order of 15 mmol/L is reached, and thereafter they fall.

In the presence of fructose, polymerization takes place in all the media. The % TYP, % GAO, and GE show an increase over those without any fructose. This fact confirms the role of fructose as an energy transfer agent. A similar effect of fructose on MMA polymerization in water and the water-methanol system has been reported

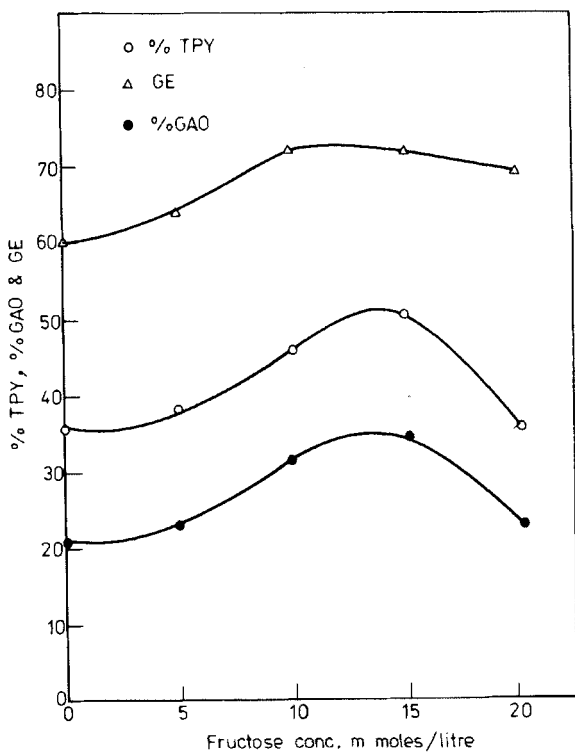


FIG. 7. Effect of fructose concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-methanol 1:1), 1:26; time, 90 min; temperature, 70°C.

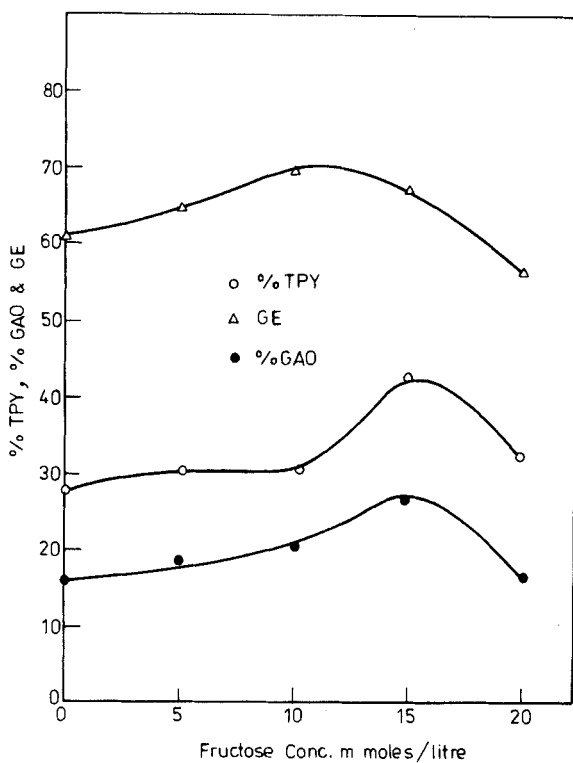


FIG. 8. Effect of fructose concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-ethanol 1:1), 1:26; time, 90 min; temperature, 70°C.

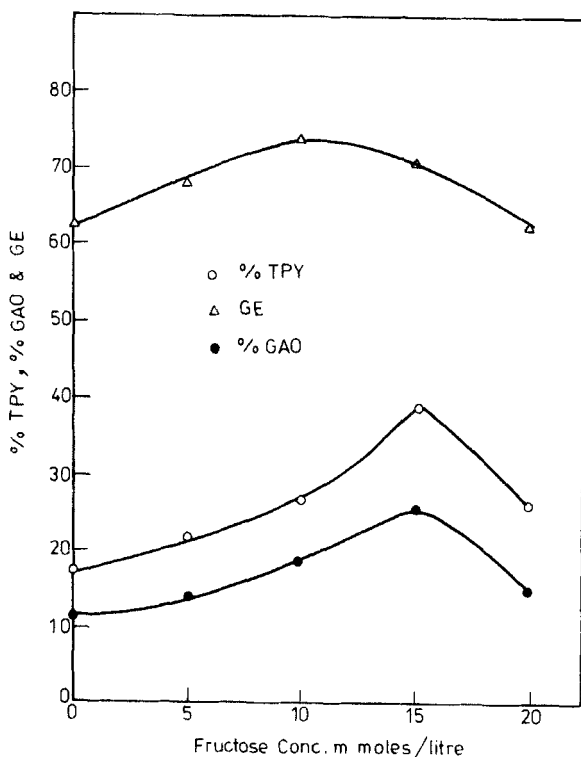


FIG. 9. Effect of fructose concentration on grafting. Nylon 6 fiber, 1 g; liquor ratio (water-n-propanol 1:1), 1:26; time, 90 min; temperature, 70°C.

by Ogiwara et al. [2]. The % TPY and % GAO increase in different media in the presence of fructose as follows: water-methanol > water-ethanol > water n-propanol.

Grafting efficiency has, however, the following order: water-n-propanol > water-methanol > water ethanol.

In all cases it is seen from Figs. 7, 8, and 9 that % TPY, % GAO, and GE increase initially, reach a maximum, and then fall. The fructose concentration at which a maximum occurs for these parameters in each medium are given in Table 2.

This shows that with an increase in fructose concentration, TPY as well as GAO and GE increase continuously at the initial stage, thus indicating that grafting is favored over homopolymerization during this period. However, with a further increase in fructose concentration beyond 10 mmol/L, the rate of homopolymerization increases at a faster rate (which is common in a normal free radical

TABLE 2

Parameter	Fructose concentration (mmol/L)		
	Water-methanol	Water-ethanol	Water-n-propanol
% TPY	15	15	15
% GAO	15	15	15
GE	10	10	10

polymerization system). Though both TPY and GAO continue to rise at this stage due to their lower growth rate relative to that of homopolymerization, GE shows a decrease.

A further increase in fructose concentration favors homopolymerization. As a consequence, the direct mutual termination between the growing polymeric MMA chains increases. Grafting site formation on the nylon 6 backbone by abstraction of an H-atom by the growing poly-MMA chain decreases, and hence GAO shows a decrease. The decrease in TPY can also be attributed to an increase in the termination rate of polymerization.

The results indicate a well-known grafting reaction scheme [7]:



The reactions which predominate are Eqs. (2) and (3).

This also indicates that the grafting sites on nylon 6 are produced mainly by abstraction of an H-atom by the growing MMA kinetic chain.

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