Effects of dextran molecular weight on graft copolymerization of dextran–methyl methacrylate

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Effects of the molecular weight of dextran on its graft copolymerization with methyl methacrylate (MMA), initiated by ceric ammonium nitrate (CAN), have been investigated. The results indicate that grafting (%), graft polymerization (%) (ψ), the overall rate constant (k') for consumption of Ce^{4+}, and branch PMMA were influenced significantly by the molecular weight of the backbone polymer dextran. The number of branch PMMA chains per dextran molecule was 0.05 ~ 0.30 for $\bar{M}_w$ 9000 dextran (D1), 0.35 ~ 0.55 for $\bar{M}_w$ 61 000 (D2), and 0.8 ~ 1.6 for $\bar{M}_w$ 196 000 (D3), respectively. The relationship between the rate of graft polymerization and $\bar{M}_w$ (the weight-average molecular weight of dextran) was expressed by the equation: $R_pg = -A \log \bar{M}_w + B$. Another linear relationship was obtained between ln (100 − ψ) and reaction time (t) for both D1 and D2 samples or ln t for D3. Detailed kinetic analysis has been made on the basis of the latter relationship. Mechanical properties were also studied on the moulded sample plates of these copolymers.

INTRODUCTION

Recently, there have been many attempts at modifying starch and cellulose to use them in graft polymerizations of vinyl compounds. Since graft polymerization of acrylamide onto poly(vinyl alcohol) in the presence of Ce^{4+} salts was reported by Mino and Kaizerman[1], many attempts have been made to graft polymerize vinyl compounds onto polysaccharides[2,3]. Most reports in this field were concerned with water-insoluble polysaccharides, and a few reports have been concerned with water-soluble polysaccharides[4,5].

Owing to their hydrophilic–hydrophobic microphase-separated structure, these copolymers may be useful as biocompatible materials, e.g. contact lenses, artificial blood vessels, and artificial bone[6–8]. With this in mind, I have reported previously graft polymerization of MMA onto dextran using CAN and characteristic properties of the resulting copolymer[7]. The influence of initiator concentration, monomer concentration and backbone polymer concentration on the polymerization were investigated[9].

Effects of the backbone polymer molecular weight on these graft copolymerizations are very important for polymer design[10,11], but these reports have been published rarely because of difficulty in measuring accurately the molecular weight of a backbone polymer. However, weight-average molecular weight ($\bar{M}_w$) of dextran can be measured accurately by using the relation between $\bar{M}_w$ and intrinsic viscosity [η] (dl g^{-1}) in aqueous solution.

In the present paper, both the contribution of molecular weight of dextran to graft polymerization and characteristic properties of the resulting copolymers have been studied.

EXPERIMENTAL

Chemicals

Methyl metahcrylate (MMA) (Katayama Chemical Co. Ltd.) was purified by distillation at 43°C under a reduced pressure of 90 mm Hg. Three types of dextran were used, with different average molecular weights: D1: $\bar{M}_w$ 9000; [η] 0.085*; D2: $\bar{M}_w$ 61 000; [η] 0.222*; D3: $\bar{M}_w$ 196 000; [η], 0.396. These dextrans were produced by Meito Sangyo Co. Ltd. and purified by a sedimentation method. The ceric ammonium nitrate (CAN) (special reagent grade, Katayama Chemical Co. Ltd.) was dissolved in 0.1 N nitric acid and the stock solution, 0.012 M in ceric nitrate, was used to prepare the polymerization suspension solution.

Polymerization procedure

Polymerization conditions to obtain maximum grafting were determined previously[9].

Dextran (60 g) was dissolved in 1650 ml of water, and then 450 g of MMA was used. During stirring, the air in the reaction vessel was replaced fully by nitrogen gas. 450 ml of the stock CAN solution was added to the solution and the mixture was stirred at a constant rate for the time needed to obtain required grafting composition. Then, 70 ml of aqueous solution of hydroquinone (0.1%) was added to terminate the reaction. The resultant mixture was poured into methanol to form a precipitate, which was washed thoroughly with boiling water, filtered, and vacuum-dried at 50°C. The crude dextran–MMA copolymer obtained was placed in a Soxhlet extractor for 30 h. Acetone was continuously added to remove the by-product homopolymer PMMA.

Isolation of PMMA from graft composition and measurement of degree of polymerization

Hydrolysis of the dextran substrate is required for analysis of the copolymer product to allow molecular weight determinations of the grafted PMMA chain. The hydrolysis conditions were the same used by Ite[2]. The graft copolymer was heated at 30°C for 2 h in 72% H_2SO_4. The solution was diluted with water to obtain 2% concentration of H_2SO_4. Boiling for 40 min followed. The solid collected by filtra-

* [η]: dl g^{-1} in H_2O, 25°C

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tion was dissolved in acetone and filtered. Methanol was then added to the resulting filtrate to form a precipitate, which was dried in a vacuum drier at 40–50°C. The isolated purified PMMA was dissolved in acetone, and its intrinsic viscosity was measured using an Ostwald viscometer at 25°C. Its molecular weight was calculated by using the following equation[12]:

$$[\eta] = 0.96 \times 10^{-4} \bar{M}_w^{0.69}$$

where $[\eta]$ is the intrinsic viscosity (dl g^{-1}) and $\bar{M}_w$ is the weight-average molecular weight of PMMA.

Rate of consumption of Ce^{4+}

Reaction rates were determined by following the absorbance of the reaction solution (Hitachi model 101 spectrophotometer). The composition of the solution ($[Ce^{4+}]$ = 2×10^{-3} M, [dextran] = 2%, $[HNO_3]$ = 0.017 N) was similar to that under the polymerization conditions. Absorbance was measured at 25°C in a 0.5 x 1 cm spectrophotometer cell. Reactant solutions were purged with nitrogen before mixing. The wavelength at which absorbance was followed, 380 nm, was chosen to give a reasonably large initial absorbance.

Material tests and water absorption

A 1 mm thick sheet sample was shaped at 200°C to 80 kg cm^{-2} gauge by a press (26 tons, Toho Press Co. Ltd.). The sheet was used in the following tests:

(a) Tensile strength (kg cm^{-2}). A rectangular sample with a width of 12.7 mm was used. Tensile strength was measured using an Autograph IM 500 (Shimadzu Seisakusho Ltd.). The testing speed was 5 mm min^{-1}, the testing temperature was 23°C, and the interchuck distance was maintained at 50 mm.

(b) Contact angle. A contact angle meter was used (Kyowa Kagaku Company). A water drop (about 0.02 ml) was prepared by a microsyringe and was brought into contact with the surface of the sample. 30 s after contact, the water drop was photographed, and h and x (shown in the following equation) were measured. The contact angle (θ) was calculated from the following equation:

$$\theta = 2 \tan^{-1} h/x$$

where x is the radius of the contact area between the water drop and the sample plate, and h is the height of the water drop in contact with the sample plate. Measurements were taken at 20°C.

(c) Water absorption (%). A 25 x 7.5 mm sample was dried for 24 h in air at 50°C, and then allowed to cool. After weighing, the sample was put into distilled water at room temperature for 24 h. The sample was removed from the water, wiped lightly with a cloth, and its weight was measured again. The water absorption (%) was determined by weight difference.

THEORY

Ceric ions complex reversibly with alcohols and glycols. The disproportionation of the complexes is the rate-determining step of the reaction[13–15]. Mino and Kaizerman have also shown that the oxidation–reduction proceeds via free radicals, capable of initiating vinyl polymerization[1]. The elementary reactions considered from the experiment are as follows:

Initiation

$$D + Ce^{4+} \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k_1} D\cdot + Ce^{3+} + H^+ \quad (1)$$

$$D\cdot + M \xrightarrow{k_2} DM\cdot \quad (2)$$

$$D\cdot + M \xrightarrow{k_3} D' + M\cdot \quad (3)$$

Propagation

$$DM\cdot + M \xrightarrow{k_5} DM_n\cdot \quad (4)$$

Termination

$$DM_n\cdot + M \xrightarrow{k_5} \text{copolymer} + M\cdot \quad (5)$$

$$DM_n\cdot + DM_n\cdot \xrightarrow{k_6} \text{copolymer} \quad (6)$$

$$DM_n\cdot + M_n\cdot \xrightarrow{k_7} \text{copolymer} \quad (7)$$

$$M_n\cdot + M_n\cdot \xrightarrow{k_8} \text{homopolymer} \quad (8)$$

$$DM_n\cdot + Ce^{4+} \xrightarrow{k_9} \text{copolymer} + Ce^{3+} + H^+ \quad (9)$$

where D, Ce^{4+}, and M are the concentrations of dextran, tetravalent cerium, and MMA, respectively.

From equation (1)

$$\text{complex} = K[D][Ce^{4+}] = \frac{K[D]}{1 + K[D]} [Ce^{4+}]_T \quad (10)$$

where $[Ce^{4+}]_T$ is the total tetravalent cerium concentration and K is the equilibrium constant. From equations (1), (2) and (3), the rate of formation of free radicals in dextran becomes:

$$d[D\cdot]/dt = k_1 K[D][Ce^{4+}] - (k_2 + k_3)[D\cdot][M] \quad (11)$$

At the steady state, its rate change is zero or $d[D\cdot]/dt = 0$.

Then, since:

$$[D\cdot] = k_1 K[D][Ce^{4+}]/(k_2 + k_3)[M] \quad (12)$$

from equations (2), (5), (6), (7) and (9) the rate of formation $[DM\cdot]$ becomes:

$$d[DM\cdot]/dt = k_2[D\cdot][M] - [DM\cdot](k_5[M] + k_7[M\cdot] + k_9[Ce^{4+}] + k_6[DM\cdot]) \quad (13)$$

Substituting equation (12) in equation (13) to eliminate $[D\cdot]$, we obtain with the steady-state approximation:

$$[DM\cdot] = k_1 k_2 K[D][Ce^{4+}]/(k_2 + k_3)(k_5[M] + k_7[M\cdot] + k_9[Ce^{4+}] + k_6[DM\cdot]) \quad (14)$$

As the propagation reaction is shown by equation (4), the rate of propagation is given by:

$$-d[M]/dt = k_4[DM\cdot][M] \quad (15)$$

Thus:

$$-d[M]/dt = k_1k_2k_4K[D][Ce^{4+}][M]/(k_2 + k_3)(k_5[M] + k_7[M\cdot] + k_9[Ce^{4+}] + k_6[DM\cdot]) \quad (16)$$

If the termination step is presented mainly by equation (5), the termination would be shown to be predominantly by chain transfer of the polymeric radical to monomer as:

$$k_5[M] \gg k_7[M\cdot] + k_9[Ce^{4+}] + k_6[DM\cdot] \quad (17)$$

Equation (16) becomes:

$$-d[M]/dt = k_1k_2k_4K[D][Ce^{4+}]/k_5(k_2 + k_3) \quad (18)$$

In the presence of excess substrate, the disappearance rate of $[Ce^{4+}]_T$ shows *pseudo first order* with respect to the total Ce^{4+} concentration:

$$-d[Ce^{4+}]_T/dt = k'[Ce^{4+}]_T \quad (19)$$

where:

$$k' = k_1\frac{K[D]}{1 + K[D]} \quad (20)$$

As the experiment gave $k't \ll 1$, by rearranging and integrating equations (18) and (19), and assuming that [D] is constant, we obtain:

$$[M] - [M_0] = -k_1k_2k_4K/k_5(k_2 + k_3)(1 + K[D])\cdot[Ce_0^{4+}]_T[D]t \quad (21)$$

or:

$$\psi = -100k_1k_2k_4K/k_5(k_2 + k_3)(1 + K[D])[M\cdot]\cdot[Ce_0^{4+}]_T[D]t \quad (22)$$

where $[M\cdot]\cdot[Ce_0^{4+}]_T$, and ψ are the initial concentration of MMA, total ceric ion, and graft polymerization (%), respectively. If a plot of ψ *versus* t gives a straight line, the termination must be caused by equation (5).

In the case of bimolecular termination as in equation (6), assuming that:

$$k_6[DM\cdot] \gg k_5[M] + k_7[M\cdot] + k_9[Ce^{4+}] \quad (23)$$

equation (16) becomes:

$$-d[M]/dt = (k_1k_2k_4^2K/k_6)^{1/2}/(k_2 + k_3)^{1/2}\cdot[M][D]^{1/2}[Ce^{4+}]^{1/2} \quad (24)$$

By rearranging and integrating equations (10), (19) and (24), we obtain:

$$\ln(100 - \psi) = -\sqrt{(k_1k_2k_4^2)/k_6(k_2 + k_3)(1 + K[D])\cdot([D][Ce_0^{4+}]_T)}\,t + 4.6 \quad (25)$$

If the termination is caused by bimolecular termination as in equation (6), a plot of $\ln(100 - \psi)$ *versus* t must give a straight line.

If a termination step can be shown as in equation (7), the termination would be caused by bimolecular termination between the graft polymeric radical and the homopolymeric radical. Assuming that:

$$k_7[M\cdot] \gg k_5[M] + k_9[Ce^{4+}] + k_6[DM\cdot] \quad (26)$$

equation (16) becomes:

$$-d[M]/dt = k_1k_2k_4K/(k_2 + k_3)k_7\cdot[D][Ce^{4+}][M]/[M\cdot] \quad (27)$$

with the formation rate of monomeric and homopolymeric radical, we obtain:

$$d[M\cdot]/dt = k_3[D\cdot][M] - k_8[M\cdot][M\cdot] - k_7[DM\cdot][M\cdot] \quad (28)$$

Because of their high concentration we may not assume that $[M\cdot]$ reaches a steady state in the experiment within a short time. Assuming $k_2 < k_3$, $[M\cdot]^2 \ll 1$, and $k't \ll 1$, by integrating and rearranging equation (28) we obtain:

$$[M\cdot] = k_1K(k_3 - k_2)/(k_3 + k_2)\cdot[D][Ce^{4+}]t \quad (29)$$

Substituting equation (29) in equation (27) and integrating, we obtain:

$$\ln([M]/[M_0]) = -k_2k_4/k_7(k_3 - k_2)\cdot\ln t + 2.3\,k_2k_4/k_7(k_3 - k_2) + 4.6 \quad (30)$$

or:

$$\ln(100 - \psi) = -k_2k_4/k_7(k_3 - k_2)\cdot\ln t + 2.3\,k_2k_4/k_7(k_3 - k_2) + 4.6 \quad (31)$$

If termination is caused by bimolecular collision between the graft polymeric radical and homopolymeric radical, a plot of $\ln(100 - \psi)$ *versus* $\ln t$ must yield a straight line of slope $-k_2k_4/k_7(k_3 - k_2)$.

If the termination step can be written as in equation (9), the termination would be shown to be predominantly by redox reaction of the polymeric radical with ceric ion. We may ignore other terminations. Thus:

$$k_9[Ce^{4+}] \gg k_6[DM\cdot] + k_5[M] + k_7[M\cdot] \quad (32)$$

Equation (16) becomes:

$$-d[M]/dt = k_1k_2k_4K/k_9(k_2 + k_3)\cdot[D][M] \quad (33)$$

As the concentration of uncomplexed alcohol in dextran is large, we can assume that [D] is constant. By rearranging and integrating equation (33):

$$\ln(100 - \psi) = -k_1k_2k_4K/k_9(k_2 + k_3)\cdot[D]t + 4.6 \quad (34)$$

If $\ln(100 - \psi)$ becomes a linear function of time (t), the termination may be represented by equation (9).

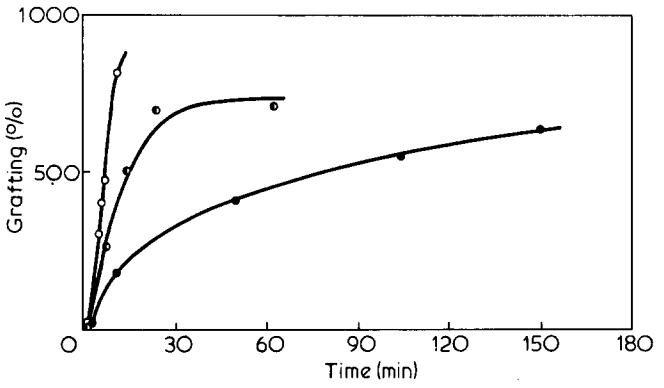


Figure 1 Grafting (%) *versus* reaction time. Backbone polymer dextran: ○, D1, $\bar{M}_w$ 9000; ◐, D2, $\bar{M}_w$ 61 000; ●, D3, $\bar{M}_w$ 196 000

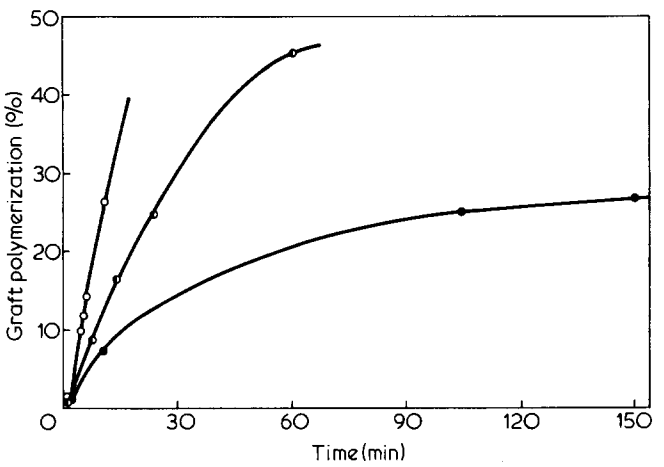


Figure 2 Graft polymerization (%) *versus* reaction time. Backbone polymer dextran: ○, D1, $\bar{M}_w$ 9000; ◐, D2, $\bar{M}_w$ 61 000; ●, D3, $\bar{M}_w$ 196 000

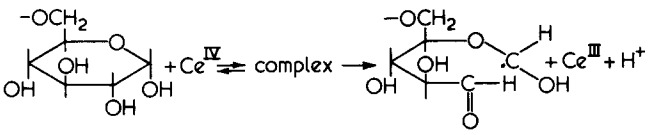
RESULTS AND DISCUSSION

Grafting (%) and graft polymerization (%)

In *Figures 1* and *2*, the relations of the grafting (%)* and the graft polymerization (%)** with reaction time are illustrated for samples D1, D2 and D3, respectively.

Graft polymerization of a vinyl monomer with polysaccharides under a redox-system initiates from *cis*-1,2-glycol function at the ends of the saccharides in preference to other mechanisms[5,16] and polymerization of MMA alone initiated by CAN may be negligible[17].

Figure 1 shows that grafting (%) increased rapidly at the beginning of the reaction when D1 sample ($\bar{M}_w$: 9 000) was one of the reactants; but gradually when D2 or D3 were reactants. Graft polymerization (%) plotted against time for the purpose of obtaining the rate of graft polymerization produces a similar profile (*Figure 2*). The results may be explained in terms of the diffusion control by the increase in viscosity of the reaction solution due to augmentation of dextran molecular weight [9,18]. It is suggested that the lower the molecular weight of dextran, the more the number of reactive functions per unit weight. This accords with the interpretation of other graft polymerizations proposed by Wallace *et al.*[5]; that polymerization is initiated mainly by the breakdown of coordination complexes of ceric ions with 1,2-glycol groups on the ends of the dextran chains. There are three such functional glycol neighbours in a terminal pyranose ring, so that three different modes of ring cleavage are possible. Homolytic bond fission between C_1 and C_2 may be most preferable, taking into account both *cis*-orientation for two hydroxyl groups[19] and powerful electron withdrawal ability for ether oxygen:



(35)

The polymerization is initiated by a ceric ion–alcohol redox system by way of an intermediate complex[9].

Grafting (%) and molecular weight of branch PMMA

Curves of grafting (%) *versus* molecular weight of the branch PMMA are illustrated in *Figure 3* for samples D1, D2 and D3. The molecular weight of the branch PMMA increases the higher the molecular weight of the backbone polymer dextran at fixed grafting (%). The molecular weight of branch PMMA and initial dextran balance one another. This suggests that the growth of the branch PMMA may progress on the backbone polymer dextrans, and that, under conditions where MMA monomer were coiled round the surface of a dextran molecule, the polymerization would proceed along the random coil formed by large dextran molecule. The number of branch PMMA chains per dextran molecule on these copolymers derived from *Figure 3* was 0.05 ~ 0.30 for D1, 0.35 ~ 0.55 for D2, and 0.8 ~ 1.6 for D3 respectively***. The above results show that the number of these branch PMMA chains grows increased grafting (%) and dextran molecular weight, and that the structures of

* Grafting (%) = (weight of monomer grafted/weight of dextran in the copolymer) X 100

** Graft polymerization (%) = (weight of monomer grafted/weight of total monomer) X 100

*** The number of branch PMMA chains per dextran molecule = (molecular weight of dextran/molecular weight of branch PMMA) X grafting (%)/100

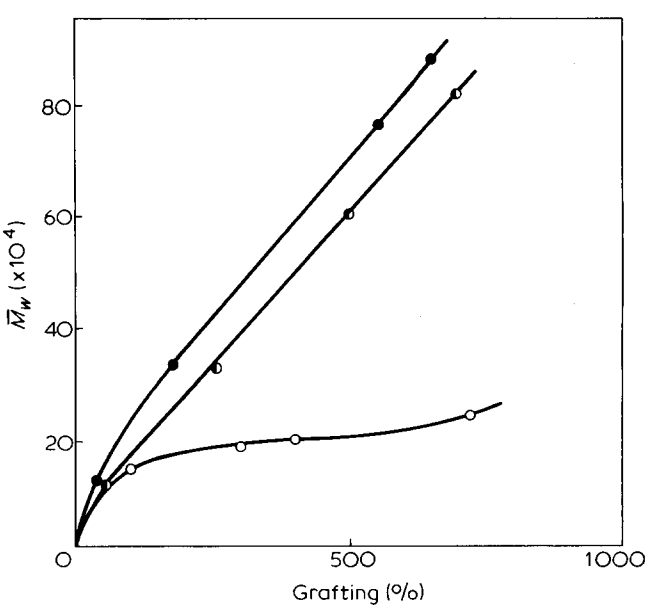


Figure 3 Relation between grafting (%) and the molecular weight of the branch PMMA. Backbone polymer dextran: ○, D1, $\bar{M}_w$ 9000; ◐, D2, $\bar{M}_w$ 61 000; ●, D3, $\bar{M}_w$ 196 000

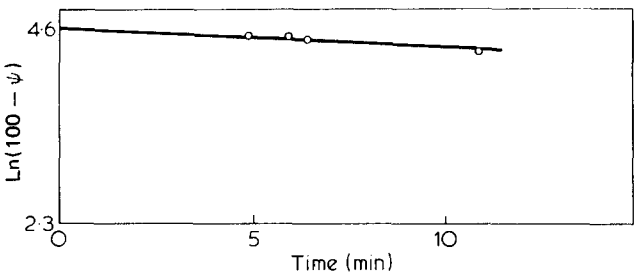


Figure 4 Plot of ln(100 − ψ) *versus* reaction time (*t*) for D1 ($\bar{M}_w$ 9000). ψ = graft polymerization (%)

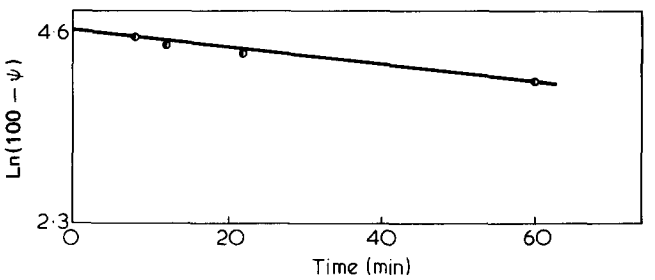


Figure 5 Plot of ln (100 − ψ) *versus* reaction time (*t*) for D2 ($\bar{M}_w$ 61 000). ψ = graft polymerization (%)

these copolymers are different from one another.

Figures 4 and *5* illustrate that, with samples D1 and D2, the plot of ln(100 − ψ) *versus t* gives a straight line with intersection at 4.6. This indicates that termination is presented by equations (6) or (9) – normal termination (by mutual collision of the graft polymeric radical) or oxidative termination (by Ce^{4+}). For sample D3, the plot of ln(100 − ψ) *versus* ln*t* yields a straight line of slope 0.1 and intersection (4.6 + 0.23) (*Figure 6*). It is deduced from this linear relationship that the termination should be presented by equation (7) – bimolecular termination between the graft polymeric radical and homopolymeric radical (or monomer radical).

The copolymer from D3 should be composed of one dextran molecular and one molecule of branch PMMA on average (1:1), because the above calculated number (0.8 ~ 1.6) from *Figure 3* may be about 1 on consideration of molecular basis. This composition must be consistent with the mechanism of termination (equation 7).

For sample D2, the polymerization may not be finished by bimolecular termination of branch PMMA, judging from the relations shown in *Figures 1* and *3*. The number of the branch PMMA chain was calculated as 0.35–0.55. On the molecular level, the result indicates that one molecule of branch PMMA might be grafted onto two molecules of dextran, cross-linked by ungrowing PMMA (on average 1:2). In addition to the initiation at the reduced terminal glucose group of D2, polymerization would occur at another glucose unit[16] in higher dextrans like D2.

In *Figure 3*, it can be seen that molecular weight of branch PMMA from sample D1 increases gradually with grafting (%) in contrast to D2 and D3. With D1, a few molecules of the starting dextran D1 would be easily cross-linked by intermediation of MMA at the beginning of the reaction. Propagation of the branch PMMA would take place on the cross-linked dextrans produced. Finally, polymerization would terminate by the above bimolecular process. Although there are uncertainties in detail, their mechanism may be deduced mainly from the present experimental results for D1.

Effect of backbone polymer dextran molecular weight ($\bar{M}_w$) on rate of graft polymerization (R_{pg})

The plot R_{pg} *versus* $\log \bar{M}_w$ yielded a straight line. The result shows that R_{pg} was a linear function of $\log \bar{M}_w$. The relation obtained can be expressed as the following equation:

$$R_{pg} = -A \log \bar{M}_w + B \qquad (36)$$

where R_{pg} is the initial rate obtained at $t = 0$ from the slope of *Figure 2*, the relation between graft polymerization (%) and time, and A and B are constant.

Equation (36) shows that the number of reactive functions per unit weight decreases with increase in molecular weight of backbone polymer but the increase in molecular weight affects the termination step negatively by increases in viscosity.

Rate of consumption of Ce^{4+} by dextran

Figure 7 shows the absorbance variation of dextran solution oxidized by Ce^{4+} with time. The overall kinetic constant (k') of consumption of Ce^{4+} by dextran, (as good *pseudo first order* kinetics (cf equation 19) were observed during the initial reaction time), was calculated from the initial slopes of the logarithm of absorbance *versus* time[15]. The overall kinetic constant (k') obtained was $6.5 \times 10^{-4} s^{-1}$ with D1; $5.0 \times 10^{-5} s^{-1}$ with D2; and $3.2 \times 10^{-5} s^{-1}$ with D3. The molecular weight of these dextrans oxidized by Ce^{4+} and that of each starting dextran were the same. The order for the rates of consumption Ce^{4+} by dextran was D1 > D2 > D3. Thus, for lower molecular weights, the rate of oxidation increases moderately. The result is consistent with that for grafting (%) (cf. *Figure 1*).

From the above results, it is concluded that graft polymerization proceeds under the influence of the molecular weight of the backbone polymer dextran.

Material tests and water absorption of the resulting copolymer

The plate of this copolymer, produced by a heat and press moulding method, was used to test water absorbing power. Water absorption reduces with increased grafting (%) and decreased molecular weight of the backbone polymer dextran at a fixed grafting (%). It may be that this water absorbing power depends on the water absorbing capacity of its dextran parts.

The tensile strength of these copolymers grew with increases in grafting (%) for each different molecular weight of backbone polymer dextran. Though a systematic effect

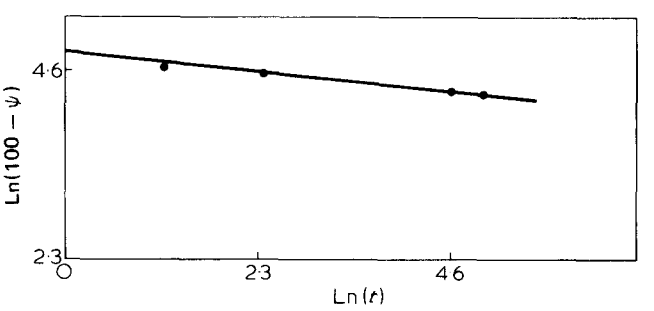


Figure 6 Plot of ln (100 − ψ) *versus* reaction time (ln*t*) for D3 ($\bar{M}_w$ 196 000). ψ = graft polymerization (%)

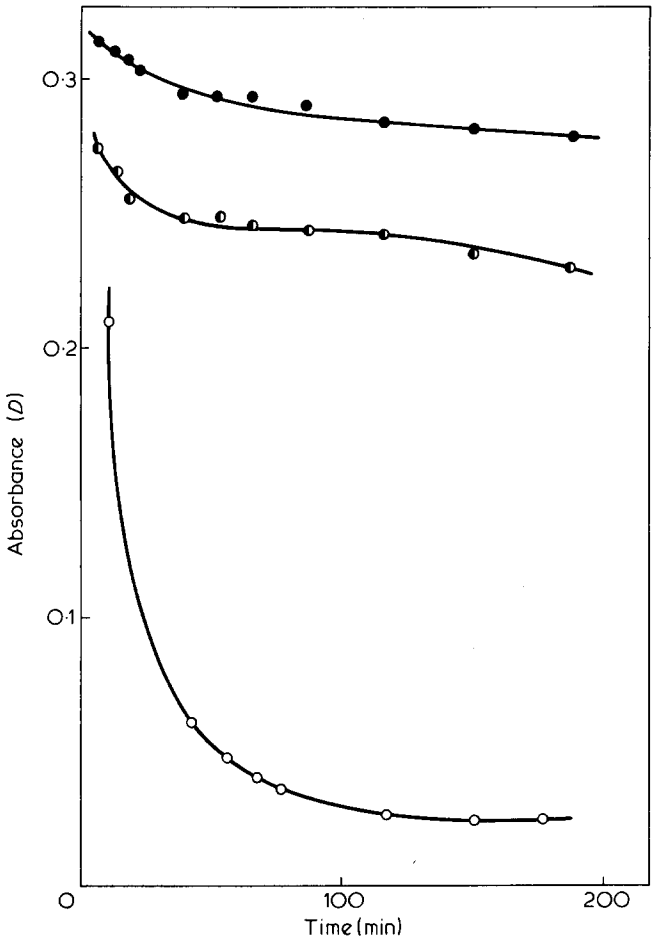


Figure 7 U.v. absorbance of dextran–Ce^{4+} solution *versus* time. Backbone polymer dextran: ○, D1, $\bar{M}_w$ 9000; ◐, D2, $\bar{M}_w$ 61 000; ●, D3, $\bar{M}_w$ 196 000

Table 1 Properties of copolymers

Samples	Tensile strength (kg cm^{-2})	Elongation	Contact angle (°)	Water absorbtion (%)	Grafting (%)
1[a]	80	0.54	66	1.4	650
2[a]	90	0.52	65	2.6	550
3[a]	86	0.42	65	7.0	175
4[b]	410	3.00	68	0.9	690
5[b]	390	2.64	65	1.6	500
6[b]	365	2.20	65	2.5	260
7[c]	293	2.20	69	1.2	720
8[c]	270	1.66	68	1.5	400
9[c]	266	1.50	68	1.6	300
PMMA[d]	507	3.90	72	0.8	–

[a] Backbone polymer dextran D3, ($\bar{M}_w$ 196 000); [b] D2, ($\bar{M}_w$ 61 000); [c] D1, ($\bar{M}_w$ 9000); [d] Sample isolated from copolymer

of the dextran molecular weight on this was not observed, it was shown that the mechanical fragility of the dextran was reinforced by PMMA grafted on dextran. *Table 1* shows that the copolymer with the backbone polymer dextran of $\bar{M}_w$ 61 000 (D2) has superior tensile strength. The relation between elongation and grafting (%) was similar to the above relation. The copolymer with the backbone polymer dextran of $\bar{M}_w$ 61 000 (D2) was superior to others with regard to elongation.

The contact angle of these copolymers was lower than for PMMA, but a systematic effect of grafting (%) and the backbone polymer dextran molecular weight was not observed.

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