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Graft Polymerization of Methyl Methacrylate Onto Gelatin

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Synopsis

In order to extend the application of grafting for the modification of natural polymers, the graft polymerization of methyl methacrylate onto gelatin by radical initiators was studied in aqueous solution at temperatures between 60°C and 80°C. Among the initiators used (peroxysulfates, α,α'-azobisisobutylonitrile, and benzoyl peroxide), potassium peroxysulfate was found to be the most efficient initiator in this particular graft polymerization. From the kinetic data with this initiator, it was shown that (1) efficiency of grafting is higher at lower temperature; (2) a sharp increase in the efficiency of grafting occurs at the later period of the polymerization at high temperature, which is attributable to the combination between homopolymer and backbone gelatin; and (3) generally, the number of branches was small and the molecular weight of the branch polymer was high in this polymerization.

INTRODUCTION

Chemical modification of natural polymers by grafting has been attracting interest from not only practical but also fundamental point of view. Graft polymerization of vinyl monomers onto natural rubbers[1] and onto cellulose[2] has been studied for a long time, and several aspects of the polymerization have been disclosed by several researchers. However, comparatively little information has been so far reported regarding the modification of proteins by graft polymerization, though the grafting onto wool[3] and collagen[4] has been studied because of its practical importance and interest.

In the present investigation, we studied the graft polymerization of methyl methacrylate (the most commonly used monomer in the study of graft polymerization onto natural polymers) onto gelatin with several radical initiators with intention of extending the applicability of the graft polymerization to modify other proteins. Although gelatin is a well-known and commonly used protein, the graft polymerization onto it has not yet been reported, probably because of its complex chemical structure composed of several constituents such as glycine, proline, hydroproline, and some other minor components. Gelatin is soluble only in hot water, which is not a good solvent for poly(methyl methacrylate). Therefore, the present polymerization system is nec-

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essarily heterogeneous and is not simple enough for studying the mechanistic aspect of reactions involved. The primary aim of the investigation is to seek proper conditions for the grafting of methyl methacrylate onto gelatin by radical initiators.

EXPERIMENTAL

Materials

Gelatin made from cow bones was supplied from Nihon Hikkaku Co.; its number-average molecular weight was 90,000–110,000. Methyl methacrylate was washed with a saturated aqueous solution of acid sodium sulfate, with an aqueous solution of sodium chloride, and with water, dried over calcium chloride and distilled under a reduced pressure under a flow of nitrogen gas. Initiators of analytical grade (potassium peroxysulfate, KPS; sodium peroxysulfate, SPS; ammonium peroxysulfate, APS; α,α'-azobisisobutylonitrile, AIBN; and benzoyl peroxide, BPO) were used as received without further purification.

Polymerization

Methyl methacrylate and initiator were added to an aqueous solution of gelatin, and then the solution was degassed by the freezing–pumping–thawing method and sealed in a sample tube under vacuum. Polymerization was carried out at 70°C, except when otherwise mentioned, during stirring. Generally, the polymerization system was composed of 1.0 wt-% of gelatin, $1.9\times 10^{-1}M$ (1.9 wt-%) methyl methacrylate, and $8.0 \times 10^{-4}M$ initiator, which gave a pH value of 6.4.

Analysis of Products

After the polymerization, the solution was mixed with a large quantity of methanol. Precipitated products were filtered, dried under reduced pressure, and weighed to determine the total conversion (conversion of monomer to homopolymer and graft polymer). Homopolymer was obtained by extracting for 24 hr in hot acetone from the precipitated products. Unreacted gelatin was separated from the residue by extracting with boiling water for 12 hr. The extraction times were so determined that further extractions did not change the results. The grafted gelatin was hydrolyzed with 6*N* hydrochloric acid at 100–110°C for 20 hr. Poly(methyl methacrylate) is known to be resistive against hydrolysis with acids and was found to show its own infrared spectrum after being treated with 6*N* hydrochloric acid at 100–110°C for 9 hr.[5] The precipitates were filtered, washed with water and methanol, purified by dissolving in acetone, reprecipitated in methanol, dried under reduced pressure, and weighed to determine the graft yield (grafted branch polymer obtained/gelatin feeded). The molecular weight of the thus obtained grafted poly(methyl methacrylate) branches, as well as that of homopoly(methyl methacrylate), was determined by viscometric measurements in benzene at 30°C, based on the relation[6] $[\eta] = 8.69 \times 10^{-5}M_n^{0.76}$.

RESULTS AND DISCUSSION

Comparison Between Initiators

In order to determine the most efficient radical initiator for grafting onto gelatin, the graft polymerization was carried out with the following five initiators: KPS, SPS, APS, AIBN, and BPO. These initiators may be divided into two groups: the first three are soluble in water, while the last two are only slightly soluble or not at all.

The total conversion of the monomer into both homopolymer and branch polymer was examined as a function of polymerization time, as shown in Figure 1. For all the initiators, the total conversion leveled off at about 85%. This seems to be due to high viscosity of the reaction system at the later period of polymerization. The rate of conversion is dependent upon the reactivity of primary radical formed from the initiators and the rate of their decomposition as well. It appeared to decrease in the order KPS > SPS ~ AIBN > APS > BPO, at 70°C. Therefore, KPS seems to be the most efficient radical initiator for the polymerization of methyl methacrylate in aqueous solution in the presence of gelatin.

The graft yield was examined only for KPS, SPS, and AIBN, which gave an appreciable rate of conversion. The results are shown in Figure 2 as a function of time. The rate of grafting decreases in the order KPS > SPS > AIBN. Although KPS and AIBN gave almost the same ultimate total conversion, as shown in Figure 1, the graft yield attainable with these initiators is much different. It reaches to as high as 90% for the first initiator, while it only reaches to 50% for the last.

From the data shown in Figures 1 and 2, the dependence of the efficiency of grafting (grafted branch polymer obtained/total monomer converted to both branch and homopolymer) upon the total conversion was obtained as shown in Figure 3. Peroxysulfates gave a feature distinctly different from that of AIBN. In addition to the fact that peroxysulfates gave higher efficiency of grafting throughout the polymerization process, the efficiency indicates a sharp increase in the later period of polymerization by the peroxysulfates, while it remains rather unchanged in the polymerization by AIBN. AIBN is thought to be dissolved in an oil phase of the monomer, so that the primary radical may readily add to the monomer to initiate the homopolym-

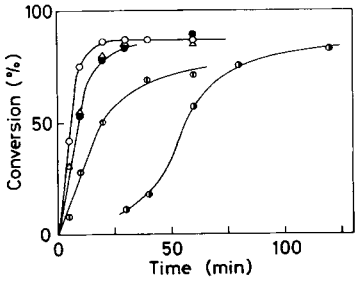

Fig. 1. Total conversion of MMA polymerization in aqueous solution in the presence of 1.0 wt-% gelatin initiated by $8.0 \times 10^{-4}M$ (○) KPS, (△) SPS, (⊙) APS, (●) AIBN, or (◑) BPO at 70°C. Concentration of monomer feed, $1.9 \times 10^{-1}M$.

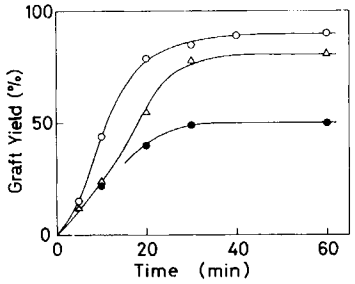

Fig. 2. Dependence of graft yield upon polymerization time at 70°C in aqueous polymerization system containing 1.0 wt-% gelatin and $1.9 \times 10^{-1}M$ MMA initiated by $8.0 \times 10^{-4}M$ (○) KPS, (△) SPS, or (●) AIBN.

erization. In the grafting onto wool by AIBN, it has been considered that the formation of the backbone radicals by the attack of the primary radical is unlikely and that the grafting is due to the recombination between propagating homopolymer radical and the backbone radical formed by chain transfer reaction.[7] On the other hand, the peroxysulfates are miscible with water, so that the primary radical from them attacks more readily gelatin solubilized in water to form a backbone radical. Although the primary radical, SO_4^-, is known to initiate the homopolymerization of vinyl monomers, it also forms a redox system with organic reductants such as alcohol and generates an organic free radical very efficiently.[8] The latter process may facilitates a mechanism of grafting in the present polymerization system: the primary radical reacts with some reducing sites in gelatin to form the backbone radical, which turns out to initiate the graft polymerization directly onto the substrate. Such mechanism was evidenced for the graft polymerization of methyl methacrylate onto poly(vinyl alcohol) by KPS.[9]

Except at the later period of the polymerization, the difference in the efficiency of grafting between peroxysulfates and AIBN is not very big but obvious. This is probably due to the solubility of the initiators and the nature of the primary radicals formed from them, as mentioned above. The sharp increase of the efficiency will be discussed in the following section. Anyhow, the above results indicate, though qualitatively, that KPS is the most efficient among the five initiators examined to initiate the graft polymerization

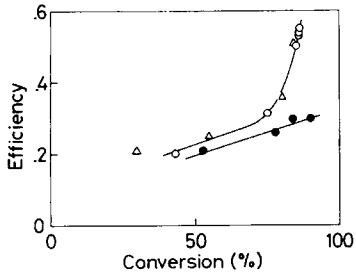

Fig. 3. Dependence of efficiency of grafting upon total conversion at 70°C in aqueous polymerization system containing 1.0 wt-% gelatin and $1.9 \times 10^{-1}M$ MMA initiated by $8.0 \times 10^{-4}M$ (○) KPS, (△) SPS, or (●) AIBN.

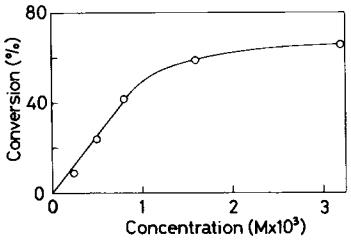

Fig. 4. Relation between initiator concentration and total conversion at the polymerization time of 5 min in aqueous polymerization system containing $1.9 \times 10^{-1}M$ MMA and 1.0 wt-% gelatin initiated by KPS at 70°C.

of methyl methacrylate onto gelatin in aqueous solution, because it gives the highest graft yield and efficiency of grafting.

Graft Polymerization by Potassium Peroxysulfate

The graft polymerization was studied more in detail for KPS as initiator. The effect of the initiator concentration is shown in Figure 4, where the total conversion at a fixed time, 5 min, is plotted as a function of the concentration. The conversion increases linearly with the increasing concentration in the range of its low values and then tends to level off. The deviation from the linearity at high concentrations is attributed to the leveling off of the time–conversion curves as shown in Figure 1. Therefore, the termination seems to be a first-order reaction with respect of the radicals involved.

Figure 5 shows the dependence of the total conversion upon the polymerization time at several temperatures. The rate of conversion increases with increasing temperature between 60° and 70°C. Although it was observed to be independent of temperature above 70°C, this may be due to the fact that the polymerization is actually completed before the high temperature of the sample solutions is attained.

The efficiency of grafting at temperature below 70°C is plotted as a function of the total conversion in Figure 6. Evidently, the efficiency of grafting becomes higher with decrease in temperature in the early period of polymerization. This implies that the primary radical more preferably attacks gelatin to form the backbone radical than adds to the monomer to initiate the ho-

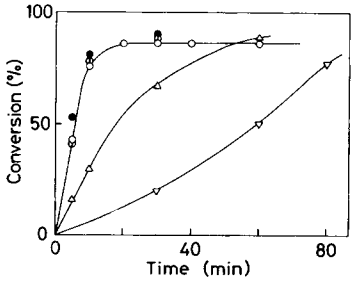

Fig. 5. Total conversion of MMA polymerization at (●) 80°C, (⊙) 75°C, (○) 70°C, (△) 65°C, or (▽) 60°C in the presence of 1.0 wt-% gelatin initiated by $8.0 \times 10^{-4}M$ KPS. Concentration of monomer feed, $1.9 \times 10^{-1}M$.

TABLE I
Representative Results of Analysis of Products of Graft Polymerization of MMA onto Gelatin in Aqueous Polymerization System Containing 1.0 wt-% Gelatine and $1.9 \times 10^{-1} M$ (1.9 wt-%) Monomer Initiated by $8.0 \times 10^{-4} M$ KPS

Temperature, °C	Time, min	Total conversion, %	Graft yield %	Efficiency of grafting	Yield of grafted gelatin, %	Number of branches	$M_n \times 10^{-5}$	
							Homo-polymer	Branch polymer
70	10	75	45	0.21	17	0.3[a]	9.0	10
70	40	86	89	0.54	26	0.5	5.0	7.0
65	60	90	75	0.43	10	0.9	8.0	8.5
60	80	77	63	0.41	6	1.2	6.5	9.5

[a] Number of poly(methyl methacrylate) branches per one gelatin backbone molecule.

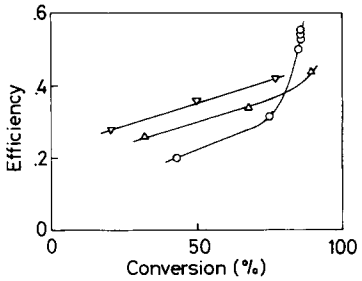

Fig. 6. Dependence of efficiency of grafting upon total conversion at (○) 70°C, (△) 65°C, or (▽) 60°C in aqueous polymerization system containing 1.0 wt-% of gelatin and $1.9 \times 10^{-1}M$ MMA initiated by $8.0 \times 10^{-4}M$ KPS.

mopolymerization at lower temperature. It is also noteworthy that, although the efficiency of grafting increases only slightly during the course of polymerization at low temperature, it shows a sharp increase at the later period of polymerization at high temperature.

Representative results of the graft polymerization with KPS are summarized in Table I. Qualitatively, three distinct features are noticeable from these results. The first, interesting from the practical point of view, is in the temperature effect on the polymerization. Although the rate of the total conversion and that of the graft yield are low at low temperature, the efficiency of grafting is high and the monomer converts more efficiently to the grafted branch polymer, as shown in Figures 5 and 6. The high efficiency of grafting results from the increase in the number of branch polymers per one backbone gelatin polymer, even though the fraction of grafted gelatin decreases, with the lowering temperature.

Secondly, the effect of the prolonged polymerization time is important at high temperature. The sharp increase in the efficiency of grafting shown in Figure 6 is accompanied by an increase in the number of branch polymers and the decrease in the molecular weight of both branch and homopolymer. One of the possible interpretations is that the primary radical attacks poly(methyl methacrylate) as well as backbone gelatin at high temperature, resulting in the decrease in the molecular weight of both branch and homopolymer. Thus formed polymer radicals, products of chain scission of poly(methyl methacrylate), are expected to recombine with the backbone radicals in the later period of the polymerization, when the homopolymerization cannot proceed because of the absence of the monomer. Therefore, the conversion from the homopolymer into the grafted branch results in an increase in grafting efficiency.

Thirdly, it is remarkable that the number of branch polymers per one grafted gelatin molecule is small and their molecular weight is high in the present graft polymerization. Although the number of the branches should essentially be larger than unity, it was observed sometimes to be less than unity. This may have been caused by missing low molecular weight poly(methyl methacrylate) homopolymer and branch polymer during the procedure of purifying products. However, the above-mentioned feature seems to be characteristic of the present graft polymerization. The high molecular weight of the grafted branches is interpreted by heterogeneity of the poly-

merization system. When a branch poly(methyl methacrylate) grows onto gelatin, the grafted copolymer becomes insoluble but it is still swelled with the monomer. Because free radicals are mainly generated in the water phase, they react with each other but do not attack the growing chains to terminate the graft polymerization resulting in a high molecular weight of the grafted branches. The small number of the grafted branches may be attributed to the structure of gelatin, where the reductant group, —CH(OH)—, responsible for the generation of the backbone radical in reacting with the primary SO_4^- radical, is small in quantity.

In conclusion, though the graft yield is high at high polymerization temperature, the number of grafted branches reaches a high at low temperature for long polymerization times. A relatively short polymerization time at low temperature is preferable to obtain long grafted branches.

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