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Grafting to Vinylpyrrolidone Polymers and Copolymers by the Ceric Ion Method

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ABSTRACT

Polymers and copolymers of vinylpyrrolidone were investigated as grafting substrates for methyl methacrylate using the ceric ion method. Ceric ion readily initiates methyl methacrylate grafting to commercial poly(vinylpyrrolidone) (PVP) of 360,000 nominal molecular weight. The resulting graft copolymer was surprisingly found to be an ABA triblock system with PVP in the center block. This conclusion is supported by three key pieces of evidence: first, selective degradation of the PVP/MMA graft copolymer showed two PMMA grafts per PVP chain: second, blocking of what are apparently hydroxylic or glycolic PVP end groups by reaction with phenyl isocyanate rendered the PVP unreactive to ceric ion grafting; third, if the PVP is prepared by methods which preclude formation of hydroxylic end groups, the PVP is unreactive to ceric ion grafting.

Vinylpyrrolidone polymers can be made graftable via ceric

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ion if N-methacryloyl-D-glucosamine (NMAG) is incorporated as a comonomer in the PVP backbone. Regardless of the method of preparation, incorporation of NMAG provides grafting sites which are highly reactive to ceric ion. At copolymer compositions up to 10 mole % NMAG, the methyl methacrylate graft copolymers are soluble in organic solvents. Above 10 mole % NMAG, the grafting reaction leads to cross-linking and formation of intractable gels.

INTRODUCTION

Mino and Kaizerman [1a, 1b] first reported the use of cerium(IV) salts to initiate graft polymerization of vinyl monomers onto poly(vinyl alcohol). Considerable attention has since been directed toward the use of cerium(IV) salts in grafting to other hydroxyl-containing polymers, particularly cellulose [2], starch [3], and proteins [4].

The nature of the graft site in these systems is still the subject of controversy. One postulate proposes that in the case of poly(vinyl alcohol) [5] and cellulose [1, 6] substrates, initiation occurs via disproportionation of a coordinated complex between ceric ion and 1,2-glycol units present in the substrate. Simultaneous carbon–carbon bond cleavage of the glycol leads to block polymer formation in the case of poly(vinyl alcohol) substrates [5, 7]. Isolation of adipaldehyde as a major product upon oxidation of cyclohexane 1,2-diol with ceric ammonium nitrate [8] provides strong support for this mechanism. Other studies propose the participation of the hemiacetal reducing end of cellulose [9, 10], and carbonyl groups present in poly(vinyl alcohol) [7], and oxidized cellulose [11] in graft site generation.

Ceric ion grafting to polymers containing reducing groups other than hydroxyl has received scant attention. The Mino and Kaizerman patent [1b] claims the use of polymeric reducing agent substrates containing hydroxyl, amine, thiol, ketone, amide, acid, ester, acetal, and aldehyde groups for the preparation of graft and oligio-block polymers. A preparation of poly(vinyl pyrrolidone-g-acrylonitrile) is presented. Although the structure of the graft polymer is not disclosed, poly(vinyl pyrrolidone) is classified as a polymeric ketone, implying participation of the lactam carbonyl in grafting.

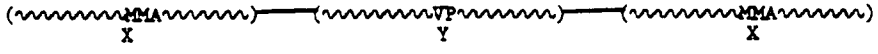
In this paper we describe the synthesis and characterization of graft polymers derived from poly(vinyl pyrrolidone) and copolymers of vinyl pyrrolidone with certain graft-reactive comonomers. Chemical and spectroscopic analyses were utilized to obtain information pertaining to the structure and location of the graft sites.

RESULTS AND DISCUSSION

Poly(vinyl pyrrolidone-g-methyl methacrylate) (PVP-g-MMA) was prepared by ceric ion initiated graft polymerization of methyl methacrylate (MMA) onto poly(vinyl pyrrolidone) (PVP) or vinyl pyrrolidone (VP) copolymers containing a minor proportion of a graft-reactive comonomer. The ceric ion method was particularly useful in these studies in that graft copolymer was obtained essentially free of poly(methyl methacrylate) (PMMA) homopolymer. Acetone extraction experiments indicated that conversion of MMA to homopolymer was less than 3% in all cases.

Type I PVP-g-MMA was prepared by ceric ion grafting of MMA to commercial PVP (GAF Corp., PVP K-90, nominal mol wt 360,000) at room temperature. Type I polymers with compositions ranging from 3 to 95 mole % MMA were readily prepared by varying the PVP:MMA charge ratio.

Chemical and spectroscopic studies of Type I polymers indicated surprisingly that grafting occurred virtually exclusively at the PVP chain ends, resulting in the ABA triblock structure depicted below. Molecular weights of X and Y for a Type I polymer containing 80 mole % MMA, for example, were found to be 5 to 7×10^5 and 3×10^5, respectively.



Type I PVP-g-MMA

The triblock structure of Type I polymers is proposed on the basis of the following evidence:

1. Selective degradation experiments indicated that Type I polymers were composed of two PMMA graft chains per PVP backbone. The PMMA graft chains were isolated quantitatively by nitric acid degradation of Type I polymers. IR and elemental analyses confirmed the purity of the isolated PMMA chains. Graft polymer compositions calculated from degradation data were in excellent accord with results obtained by other methods. Control experiments verified the fact that PMMA homopolymer was not degraded under the reaction conditions employed. The molecular weight of the isolated PMMA was calculated from viscosity data utilizing [12]

$$[\eta]^{25^\circ}_{CHCl_3} = 5.81 \times 10^{-5}\ \overline{M}_n^{0.79} \qquad (1)$$

The number of PMMA grafts per PVP backbone, N, was estimated from the molecular weight data by use of Eq. (2). Values of N determined in this manner ranged from 1.8 to 2.2 for several copolymers:

$$N = [(S/C) - S]/G \quad (2)$$

where S = DP of PVP backbone, C = copolymer composition (mole fraction VP), and G = DP of PMMA graft chains.

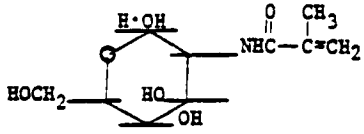
2. Commercial PVP appears to contain hydroxylic chain end groups. Reaction of commercial PVP with phenyl isocyanate afforded a substrate polymer that failed to graft in the presence of ceric ion and MMA. The IR spectrum of a low molecular weight PVP (GAF Corp., PVP K-15, nominal mol wt 10,000) exhibited a weak carbamate absorbance at 1725 cm^{-1} after reaction with phenyl isocyanate.

3. The reactivity of PVP toward ceric ion initiated grafting is dependent upon the polymerization conditions employed in the preparation of the substrate polymer. PVP prepared in aqueous solution using hydrogen peroxide as initiator is readily grafted. PVP prepared in benzene or N-methyl pyrrolidone solution using AIBN as initiator failed to graft in the presence of ceric ion and MMA. The early literature suggests that hydrogen peroxide initiated aqueous polymerization may be used to prepare commercial PVP [13].

Ceric ion initiated MMA polymerization occurs readily in the presence of low molecular weight commercial PVP K-15. Extraction experiments, however, indicated that the product is a mixture of the respective homopolymers. One can speculate that glycol-type chain transfer agents may be employed commercially to prepare low molecular weight PVP, resulting in 1,2-diol chain ends. By analogy to the mechanism proposed for ceric ion grafting to poly(vinyl alcohol) [5, 7], carbon—carbon bond cleavage could lead to PMMA homopolymer formation.

In attempting to further characterize the graft sites on commercial PVP, several N-substituted pyrrolidones were examined as model graft substrates. Under grafting conditions where PVP substrate resulted in 70 to 95% MMA conversion, N-methyl-, N-cyclohexyl-, N-isopropyl-, and N-isobutylpyrrolidone model substrates resulted in 3 to 9% MMA conversion. MMA conversions of 1 to 3% were obtained in the absence of substrate. These results appear to confirm our belief that ceric ion oxidation does not involve radical generation along the polymer backbone or on the pyrrolidone ring. In similar experiments N-methylol- and N-ethylolpyrrolidone were examined as model chain end graft substrates. MMA conversions of 20 to 30% were observed. These results, while unfortunately inconclusive, suggest that the N-alkylol pyrrolidones may be approximate models for the chain ends of commercial PVP.

PVP-g-MMA possessing graft chains attached along the PVP backbone can be prepared by incorporating a minor proportion of graft-reactive comonomer into the PVP backbone. For this purpose we utilized N-methacryloyl-D-glucosamine (NMAG). NMAG homopolymer is reported to undergo a 1000% weight increase upon ceric ion grafting with MMA [10].



NMAG

In view of our evidence for the participation of PVP end groups in the grafting reaction, we would expect the method of preparation of VP-NMAG copolymers to similarly affect the location of MMA graft chains. Thus VP-NMAG copolymers prepared under conditions which preclude the formation of hydroxylic end groups would be expected to possess NMAG units as the sole graft-reactive sites. Conversely, VP-NMAG copolymers prepared under conditions condusive to the formation of hydroxylic end groups would be expected to contain both NMAG and chain end graft sites.

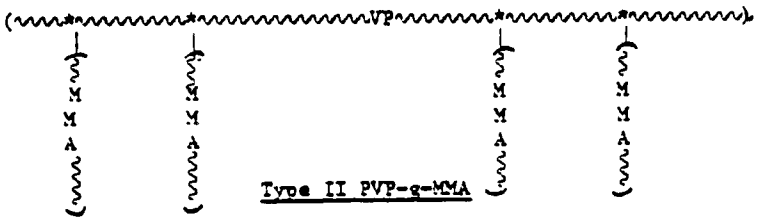
Accordingly, VP-NMAG copolymers containing 5 to 15 mole % NMAG were prepared in benzene or N-methylpyrrolidone, initiated by AIBN, and in aqueous solution initiated by hydrogen peroxide. MMA grafted readily to both types of substrate polymer in the presence of ceric ion. Backbone polymers containing 5 or 10 mole % NMAG afforded graft polymers that were fully soluble in acetic acid. Extensive cross-linking and gelation occurred upon grafting to substrates containing 15 mole % NMAG.

MMA grafting to VP-NMAG copolymers prepared in organic solvents afforded Type II PVP-g-MMA, while Type III PVP-g-MMA resulted upon grafting to VP-NMAG copolymers prepared in aqueous solution. Proposed structures for Types II and III graft polymers are depicted below where a * indicates a PMMA graft chain attached at an NMAG unit in the backbone.

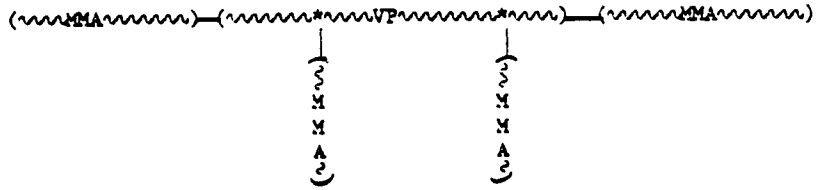
Selective degradation experiments provided support for the proposed structures of Types II and III graft polymers. Table 1 summarizes the results of our examination of the structures of Types I, II, and III graft polymers containing 77 to 90 mole % MMA.

PMMA graft chains on Type II polymers proved to be resistant to isolation by nitric acid degradation. The resistance of MMA-grafted NMAG homopolymer to selective degradation by periodic acid has been previously noted [10]. A portion of the PMMA graft chains could be isolated by prolonged alkaline degradation, however, with attendant cross-linking and gelation of the PVP backbone. Extraction of the digested graft polymer gel afforded a sufficient quantity of the PMMA graft chain for identification and characterization. As expected, an increase in the number of graft sites (NMAG content) afforded Type II polymers with increasing graft frequencies and decreasing graft chain lengths.

Nitric acid degradation of Type III PVP-g-MMA afforded a high molecular weight PMMA component and a vinylpyrrolidone backbone containing a small amount of PMMA. The former derives from the



Type II PVP-g-MMA



Type III PVP-g-MMA

end-grafted PMMA chains while the latter represents the remaining VP-NMAG backbone with PMMA chains attached at NMAG units. It appears that most (88%) of the MMA is consumed in end-grafting in the case of Type III polymers.

EXPERIMENTAL

Vinylpyrrolidone was purified by vacuum distillation from KOH pellets. The fraction boiling at 69°C (1 Torr) was collected and stored under nitrogen at -20°C. Poly(vinylpyrrolidone) K-15 and K-90, obtained from the GAF Corp., were dried over P_2O_5 in vacuo prior to use. Methyl methacrylate was washed with aqueous KOH, then water, and dried over anhydrous sodium sulfate. The fraction boiling at 97.5°C (335 Torrs) was collected and stored under nitrogen at -20°C. N-Methacryloyl-D-glucosamine (NMAG) was prepared from methacrylic anhydride and glucosamine hydrochloride as follows. A methanolic sodium methoxide solution was prepared by slowly adding 640 ml of anhydrous methanol to 6.9 g (0.3 mole atom) of freshly cut sodium. To this solution was added 64.4 g (0.3 mole) glucosamine hydrochloride. After 15 min the sodium chloride precipitate was removed by filtration and the filtrate was cooled in an ice bath. To this glucosamine solution 60.1 g (0.39 mole) of methacrylic anhydride (stabilized with methylene blue) were added dropwise over a 1-hr period. After stirring for 3 hr, the solution was warmed to room temperature and treated with activated charcoal. Ether was added to the

TABLE 1. Summary of Graft Polymer Structures

	Backbone polymer		Graft polymer composition and structure			
Polymer type	Mol wt ($\times 10^{-5}$)	NMAG content (mole %)	Composition mole % MMA	Graft site	Graft chain mol wt ($\times 10^{-5}$)	Graft frequency[a]
I	3.6	0	80	Chain ends	6.7	0.6
II	1.1	5.5	79	Backbone	2.1	2.0
II	1.2	10.0	77	Backbone	1.3	3.3
III	3.3	5.1	90	Chain ends	17.8	b
				Backbone	b	b

[a]Graft frequency = number of PMMA graft chains per 1000 backbone monomer units.
[b]Not determined; 88% of MMA grafted at chain ends, 12% onto backbone.

resulting clear solution to incipient clouding and the contents were stored overnight at ice-box temperature. Filtration, followed by drying in vacuo at 23°C, afforded N-methyacryloyl-D-glucosamine (43 g, 58% yield, mp 190 to 192°C). Reference 14, mp 193 to 194°.

Preparation of a vinylpyrrolidone-NMAG copolymer backbone utilized to prepare Type III PVP-g-MMA is described below. Backbone polymers for Type II graft polymers were prepared in a similar manner employing AIBN as initiator and benzene or N-methyl pyrrolidone as solvent. A 4-oz polymerization bottle was charged with 2.47 g (0.01 mole) of NMAG, 10.0 g (0.09 mole) of freshly distilled N-vinyl pyrrolidone, 0.1 ml 30% H_2O_2, and 50 ml boiled distilled water. Following a nitrogen purge, the bottle was capped and placed in a 40°C oil bath for 16 hr. The copolymer was isolated by precipitation of the viscous aqueous solution into acetone and purified by reprecipitation from DMF solution into acetone. Following drying in vacuo at 40°C, the polymer was obtained as a hard white solid (8.6 g, 70% yield). IR analysis indicated a composition of 11.8 mole % NMAG. The polymer exhibited an intrinsic viscosity of 1.2 dl/g in water and 25°C and afforded flexible films on casting from water.

Copolymer molecular weights were calculated from intrinsic viscosity data and appropriate viscosity molecular weight relationships for poly(vinylpyrrolidone) [15].

Compositional Analysis of VP-NMAG Copolymers. Copolymer compositions were determined from the IR spectra of films cast from 0.5% aqueous solution directly on silver chloride plates or in the form of free films cast on aluminum foil. Compositions were determined by calculating the ratio (R) of the transmittance peak heights at 1280 and 1365 cm^{-1} using a horizontal baseline at 1340 cm^{-1}. The copolymer compositions were then obtained by means of a calibration curve of mole % NMAG vs R (obtained from the spectra of known homopolymer mixtures).

Ceric ion initiated grafting of MMA to PVP or VP-NMAG copolymers employed similar procedures. The following example describes the preparation of a Type II polymer. A three-necked, 250 ml flask fitted with stirrer, condenser, and nitrogen purge tube was charged with 125 ml boiled, distilled water and 2.81 g of a VP-NMAG copolymer which contained 10 mole % NMAG. After a 60-min nitrogen purge, 8.0 g distilled methyl methacrylate was injected. After an additional 10 min purge a solution of 0.270 g ceric ammonium nitrate in 5 ml of 1 N HNO_3 was injected (equivalent to 0.025 mole catalyst/mole of repeat unit in the backbone). After 3 hr at room temperature the white suspension was diluted with an equal volume of methanol and precipitated into ether. The solids were then collected and dried in vacuo at 40°C. The yield was 9.8 g of polymer containing 80.5 mole % MMA by IR analysis. Type II and III graft polymers containing 10 mole % NMAG in the backbone were soluble in acetic acid. Backbone polymers containing 15 mole % NMAG were severely cross-linked during the grafting reaction.

All graft polymers were subjected to consecutive extractions with methanol and acetone to remove traces of the respective homopolymers.

Graft copolymer compositions were determined from the IR spectra of films cast from acetic acid solution. Compositions were determined by calculating the ratio (R) of the transmittance peak heights at 1740 (ester) and 1675 (amide) cm^{-1} using a baseline drawn between the spectrum intercepts at 1600 and 1800 cm^{-1}. The compositions were then determined by means of a calibration curve of mole % VP vs R (obtained from the spectra of known homopolymer mixtures).

Nitric Acid Degradation of Type I PVP-g-MMA. A 3.0-g sample of Type I PVP-g-MMA, containing 20.0 mole % VP, was digested in 35% nitric acid for 50 hr at 115°C, affording two products. Product I was insoluble in the reaction medium but soluble in chloroform. Product II, isolated from the reaction filtrate, was identified as poly(vinylpyrrolidone) by comparison of its IR spectrum with an authentic sample.

Product I (2.35 g) was identified as PMMA by comparison of its IR spectrum with an authentic sample. The yield of I corresponded to a graft copolymer composition of 19.95 mole % vinylpyrrolidone. The elemental analysis of I was in excellent agreement with that calculated for PMMA. Nitrogen analyses by pyrolysis and Kjeldahl techniques were 0.00 and < 0.05%, respectively.

The intrinsic viscosity of I in $CHCl_3$ at 25°C was 2.4 dl/g. The molecular weight of I, calculated from Eq. (1), was 7×10^5. The graft frequency N (Eq. 2) was thus found to be 1.8 using values of 3200, 0.20, and 7000 for S, C, and G, respectively.

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