

Graft Copolymerization onto Wool Fibers: Graft Copolymerization of Acrylic Acid onto Wool Fibers Initiated by Quinquevalent Vanadium

Gitisudha GIRI, C. N. NANDA, and Rajani K. SAMAL*

*Macromolecular Research Laboratory, Department of Chemistry,
Ravenshaw College, Cuttack-753003, Orissa, India*

(Received April 11, 1989)

ABSTRACT: Graft copolymerization of acrylic acid onto wool fibers was carried out with quinquevalent vanadium as the initiator in an aqueous medium under nitrogen atmosphere. The percentage of grafting was influenced by reaction time, temperature, concentrations of acid, monomer, initiator and base polymer. Grafting has also been carried out in the presence of various organic solvents. It has been observed that 193.7% of grafting is obtained at 55°C for [AA]=1.46 M, $[V^{+5}] = 0.025$ M, Wool=0.2 g and for a reaction time of 6 h. A suitable mechanism has been proposed for graft initiation and termination. A theoretical rate equation has been derived. The behaviour of the graft copolymers towards mineral acids and alkalis has been tested. Their tensile properties, dye-uptake ability and absorption of water and water vapour have also been examined.

KEY WORDS Defatted Wool / Initiator Effect / Monomer Effect / Temperature Effect / Solvent Effect / Tensile Modulus / Dye-Uptake /

Wool, a natural protein, called α -Keratin has significant characteristics and is used for making warm garments. With a view to enhance the durability of woollen garments and to add improved properties such as better dyeability, prevention of shrinkage and pilling, improved bacterial resistance, hydroscopicity, tensile strength, thermal stability, etc. attempts have been made since 1945 to modify wool fibers chemically. This involves functionality changes *via* etherification, esterification, urethanation, amidation, etc.¹⁻⁵; by interfacial graft condensation of polyamides,⁶⁻⁸ polyurethanes,⁹ polyureas, polyesters, polycarbonates¹⁰ *via* radical grafting of vinyl monomers involving high energy radiation. Photochemical and chemical method of initiation involving metal and non-metal ion initiators¹¹⁻³⁷ and through chemical treatments.³⁸⁻⁵¹ However, during recent years,

chemical methods of initiation of grafting involving metal and non-metal ion oxidisers, organic peroxides, hydroperoxides, aliphatic azo compounds like Ce^{+4} , V^{+5} , $Mn(IV)$, $Mn(III)$, $S_2O_8^{2-}$, HSO_5^- , H_2O_2 , $P_2O_8^{2-}$, BPO, CHP, AIBN, etc. have attracted the attention of chemists as has been reviewed by us recently.⁵² Among the chemical initiators quinquevalent V(V) has a unique identity and it is reported to oxidise a multitude of organic substrates (alcohols, acids, aldehydes, sugars, mercaptanes) in aqueous H_2SO_4 medium.⁵³ Most of such reaction proceed through a free radical path that effectively initiates vinyl polymerization. Further, quinquevalent vanadium has similar affinity towards macromolecules containing characteristic pendant groups ($-OH$, $-CHO$, $-NH_2$, $-SH$, $-COOH$, etc.) on their backbone so that the interactions of V(V) with the groups form polymer free radicals

* To whom all correspondence should be made.

that initiate grafting, as has been reported by Ikada *et al.*⁵⁴ in the grafting of MMA onto PVA with V(V).

However, scanty literature is available on the grafting of vinyl monomers onto wool fibers initiated by quinquivalent V(V),⁵⁵⁻⁵⁸ where graft copolymers show improved thermal stability, dyeability and grafting results in the light fastness of wool fibers. We have therefore been interested in studying graft copolymerization of vinyl monomers onto wool fibers using quinquivalent vanadium (V⁺⁵) as the initiator so as to improve properties such as high tenacity towards acids and alkalis, improved absorption of water and water vapours, tensile strength, dye uptake ability etc. to the fiber. The present report on grafting of acrylic acid is a part of these studies.

EXPERIMENTAL

Materials

Wool fibers were purified by continuous soxhelenation in petroleum ether. They were then washed well with warm acetone followed by distilled water and air dried. Acrylic acid (G.S.C) was purified by distillation under reduced pressure and the middle fraction was collected and used for all experiments. A stock solution of the initiator "V(V)" (0.1 M) was prepared by dissolving 2.925 g of NH₄VO₃ in 5 M H₂SO₄ and strength of the stock solution was determined by cerimetry. All other reagents were of B.D.H. (AR) grade and used after purification by standard methods. Graft copolymerization was carried out in a specially designed reaction vessel having outlet and inlet system, for deaeration. The defatted wool fibers (0.2–1.0 g) were immersed in a mixture containing water and the required amount of acrylic acid. The reaction vessels were deaerated by passing oxygen-free nitrogen for one hour and were then sealed airtight by rubber cappings. The vessels were then kept in a constantly shaking thermostat at the desired

temperature, till the mixture attained thermal equilibrium after which the required amount of initiator was injected through the rubber capping and the reaction was carried out for the desired time. The homopolymers were extracted by repeated boiling of the graft copolymers in warm distilled water and methanol till the washings did not yield any precipitate.

From the weight of the graft copolymers and parent fiber the percentage of grafting was calculated as follows.

$$\text{Percentage of grafting} = ((X - Y)/Y) \times 100$$

where

X = Weight of the graft copolymer

Y = Weight of the original base polymer

Tensile Modulus

The tensile modulus at the break of the parent fiber and graft copolymers was determined by a "Dutrons" Tensile Tester, Brand—20 kgf capacity, the details of which are cited in the properties section of this manuscript.

Dye-Uptake

The dye-uptake ability of the grafted samples was assessed using "Sandocryl Golden Yellow B-GRL 300%" dye and compared with that of the parent fiber.

RESULTS AND DISCUSSION

Acrylic acid was graft copolymerized with defatted wool fibers initiated by quinquivalent vanadium either alone or in the presence of dil. H₂SO₄ under identical reaction conditions. The results of such copolymerizations are presented in Table I. Table I shows that acid (H₂SO₄=0.5 M) enhances the percentage of grafting. This enhancement of percentage of grafting may be attributed to increase in the oxidation potential of quinquivalent vanadium due to the production of more active VO₂⁺ species and/or V(OH)₃²⁺. These vanadium spe-

Table I. Variation in percentage of grafting at different times
Effect of initiators: wool=0.2 g; [AA]=1.46 M; temp=50°C; [Initiator]=0.01 M.

[Initiator]	% Grafting					
	1 h	2 h	4 h	6 h	8 h	9 h
V ⁺	4.8	14.9	27.2	37.9	36.7	36.0
V ⁺ with H ₂ SO ₄ (0.5 M)	10.5	17.2	30.9	54.3	53.0	53.8

cies have been found potential oxidisers of a large number of organic substrates, whose oxidation proceeds through a free radical path.⁵³ In this case, the said vanadium species probably attacks the wool backbone at a faster rate, resulting in the generation of a large number of grafting sites. Further, increase in acid concentration (>0.5 M) still increases the percentage of grafting beyond 53.75%. In this study it was noted that even though increase in acid concentration increases the percentage of grafting to 193.7%, there still exists an optimum concentration of H₂SO₄ (0.75 M) and other reaction components ([V⁺]=0.015 M, [AA]=1.46 M, temp=45°C) at which the graft copolymer (with 46.2% grafting) having ideal properties is obtained, beyond which deterioration in the grafted samples is observed. This might be due to oxidative and hydrolytic chain cleavage of the polypeptide chain in wool backbone at higher concentrations of V⁺, H₂SO₄ and reaction temperature beyond 45°C.

i) Effects of Monomer/Polymer Ratios

The effects of the monomer/polymer (M/P) ratio on the grafting of acrylic acid onto wool fibers were studied at various monomer concentrations between 0.18 M to 1.82 M at a fixed concentration of initiator (15×10^{-3} M), H₂SO₄ (0.75 M), Wool (0.2 g) for a reaction time of 6 h at five different temperatures between 35–55°C. The percentage of grafting was found to increase steadily with monomer

concentration and temperature simultaneously (Figure 1). This enhancement in percentage of grafting may be interpreted in terms of acrylic acid concentration and its reactivity. Increase in M/P ratio increases monomer (AA) concentration at close proximity of the fiber backbone, where some of the acrylic acid molecules form a donor-acceptor complex, through interaction of their carboxyl functions with the pendent groups on wool backbone. Out of the uncomplexed monomers, those which are in the immediate vicinity of the reaction sites become acceptors of wool radicals resulting in chain initiation and thereafter they themselves become free-radical donors predominantly for uncomplexed monomers converted to stronger acceptors and neighbours than the remaining uncomplexed monomers situated a short distance away. These factors result in increase in the reactivity of the monomers thereby enhancing the percentage of grafting. Gaylord⁵⁹ and Hebeish⁶⁰ have also put forth a similar explanation for the enhancement of grafting at high monomer concentrations.

ii) Effects of Initiator Concentration

The effects of initiator concentration on grafting of acrylic acid onto wool fibers were studied at a number of initiator concentration from 0.00125 M to 0.025 M, at a fixed weight of wool fibers (0.2 g), monomer concentration (AA=1.46 M), reaction time of 6 h and at five different temperatures (35–55°C) (Figure 2). It was observed that the percentage of grafting increases with initiator concentration. The increase in percentage of grafting with initiator concentration may be ascribed to the increase in active sites on the backbone of wool fibers arising from the attack of diffused V⁺ on the polymer matrix so that grafting also may occur in the interior region of the fiber. Since the grafted fibers get deteriorated at a higher concentration of initiator, further studies were carried out at the initiator concentration of 0.015 M.

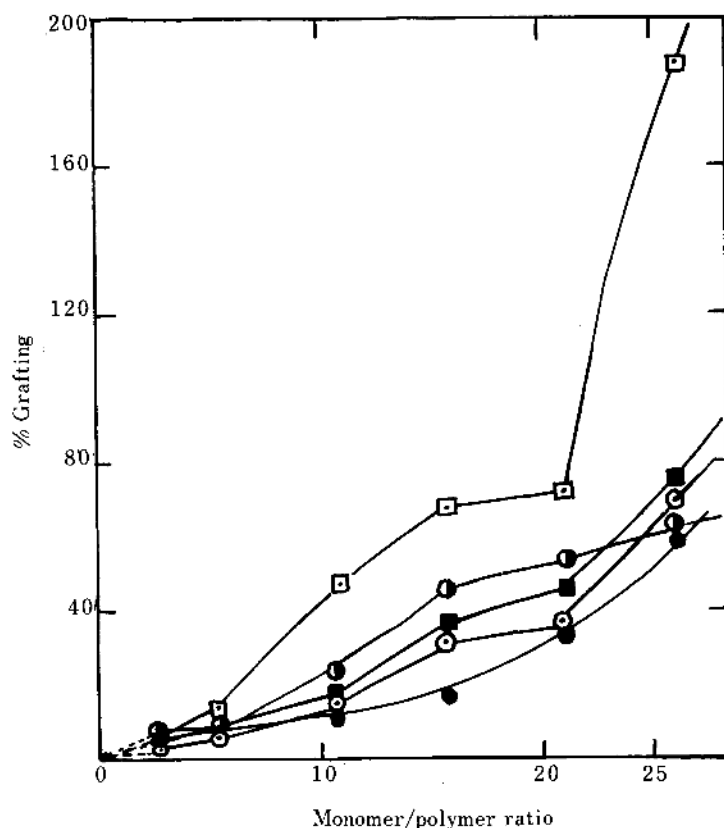


Figure 1. Variation in percentage of grafting at a fixed time. Effects of monomer/polymer ratio at different temperatures: wool = 0.2 g; $[V^{+5}] = 15 \times 10^{-3}$ M; time = 6 h. (●) $T = 35^\circ\text{C}$; (○) $T = 40^\circ\text{C}$; (■) $T = 45^\circ\text{C}$; (◐) $T = 50^\circ\text{C}$; (◑) $T = 55^\circ\text{C}$.

iii) Effects of Temperature

Graft copolymerization of acrylic acid onto wool fibers has been studied at various temperatures (35–55°C), with fixed concentration of V^{+5} (15×10^{-3} M), Wool (0.2 g) and reaction time of 6 h at different monomer concentrations (AA = 0.18–1.82 M) (Figure 3). The percentage of grafting increases with both monomer concentration and temperature. The enhancement in percentage of grafting with rise in temperature may be attributed to (i) activation of the wool backbone and $V(V)$, where facile oxidation of the former by the latter generates a large number of grafting sites at which monomer addition takes place and (ii) increase in temperature increases the rate of diffusion of AA into the fiber matrix, where

grafting is also initiated at the interior region of the wool backbone. Samal and coworkers^{61–63} made similar observations in the grafting of AM onto cellulose, Nylon-6 and silk fibers. Since the grafted fiber was deteriorated at temperature beyond 45°C, further studies have been carried out at this temperature.

iv) Effects of Solvent Composition

The effects of various organic solvents such as acetone, acetic acid, methanol, formic acid, cyclohexanone and Pyridine on the extent of grafting have been studied at various solvent compositions of (5:95–50:50 v/v) at 45°C for fixed concentrations of AA (1.46 M), V^{+5} (0.015 M). Wool (0.2 g) for a reaction time of

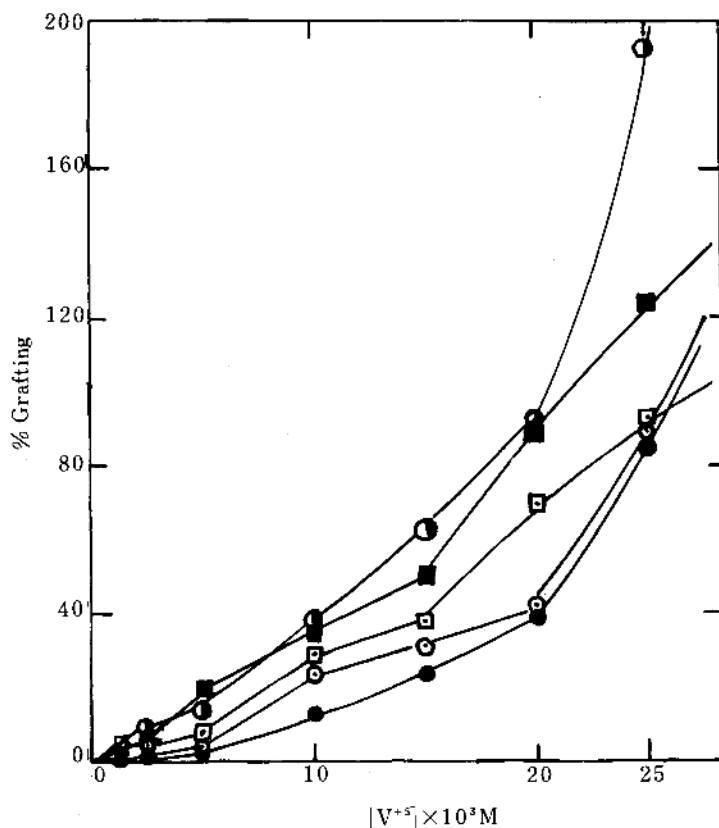


Figure 2. Variation in percentage of grafting at a fixed time. Effects of various $[V^{+5}]$ at different temperatures: wool=0.2 g; [AA]=1.46 M; time=6 h. (●) $T=35^{\circ}\text{C}$; (○) $T=40^{\circ}\text{C}$; (□) $T=45^{\circ}\text{C}$; (■) $T=50^{\circ}\text{C}$; (○) $T=55^{\circ}\text{C}$.

6 h. The effects of these solvents under the cited reaction conditions on the extent of grafting are shown in Figure 4. From the figure, it is evident that in the presence of solvents like acetone upto 20% acetic acid and methanol upto 10%, the percentage of grafting increases and then decreases. The presence of solvents like Pyridine and cyclohexanone progressively reduces the percentage of grafting, the extent being much higher in the presence of the former and at 50%, it completely inhibits the grafting reaction. Further, it has been observed that for all proportions of formic acid, the percentage of grafting is higher than the control value, even though there is an initial increase upto 10% followed by decrease in the percentage of grafting. The increase in the

percentage of grafting in the presence of formic acid may be attributed to (i) swelling of the fibers in its presence permits the monomer and the initiator to be diffused into the fiber matrix so that grafting is initiated both at the fiber surface and below the fiber surface, (ii) in addition, the swelling of the fiber also permits high accessibility of the surface of the wool fibers attack by primary radicals, creating more of free radical sites leading to graft initiation. The enhancement of percentage of grafting in the presence of the solvent like acetone, acetic acid and methanol at the cited compositions may be ascribed to the adequate amounts of solvent radicals contributing generation of greater number of grafting sites on the wool backbone which add a large number

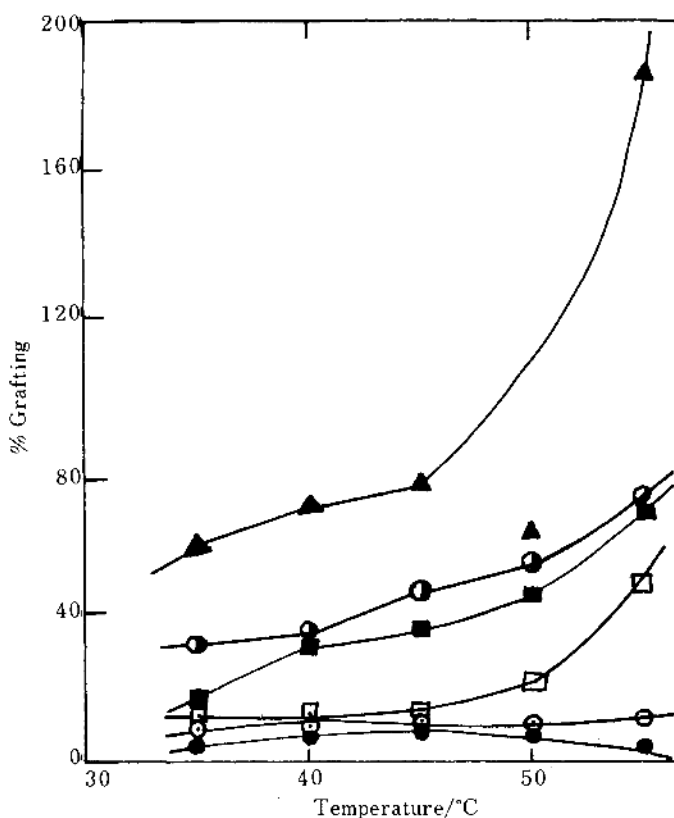


Figure 3. Variation in percentage of grafting at a fixed time. Effects of different temperatures at various [AA]: wool = 0.2 g; $[V^{+5}] = 15 \times 10^{-3}$ M; time = 6 h. (●) [AA] = 0.18 M; (○) [AA] = 0.36 M; (◻) [AA] = 0.73 M; (■) [AA] = 1.09 M; (◐) [AA] = 1.46 M; (▲) [AA] = 1.82 M.

of monomer molecules leading to high percentage of grafting. The retardation of the rate at higher percentage of these solvents and cyclohexanone may be due to (i) the chain transfer ability of these solvents leading to premature termination of the growing grafted chains, (ii) massive formation of homopolymers by excess solvent radicals upsets the grafting, (iii) shielding of the wool radicals by a solvent cage arising from interchain hydrogen bonding of the solvent molecules as a result of which monomer addition onto grafting sites is somewhat prevented. This is consistent with the view of Kern and coworkers⁶⁴ and Palit and coworkers.⁶⁵ The retardation and/or inhibition of grafting in the presence of Pyridine may be attributed to its oxidation to

pyridine-*N*-oxide by V^{+5} , which is capable of retarding and/or inhibiting radical polymerization depending on its concentration. The oxidation of pyridine to pyridine-*N*-oxide⁶⁶ and partial/complete inhibition or retardation of radical polymerization by *N*-oxide are well recognized.⁶⁷

MECHANISM

The mechanism of graft copolymerization onto wool fibers initiated by quinivalent vanadium has been pictured as involving the initial complex formation of $V(V)$ with either the pendent groups and/or the peptide linkage of the wool fibers. The intermediate complex subsequently disproportionates in an unimo-

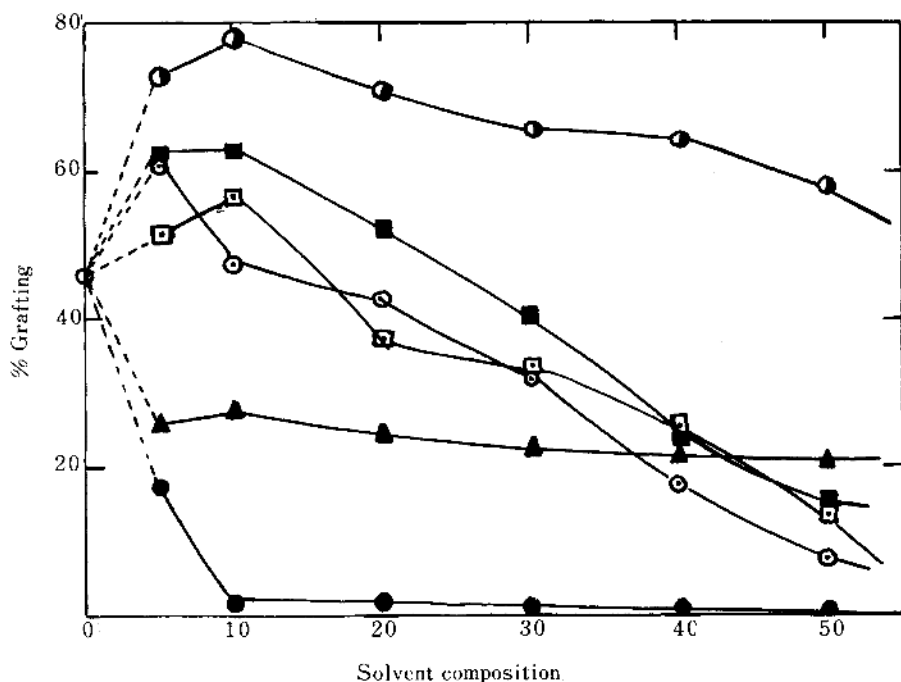
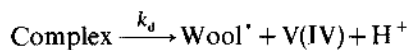
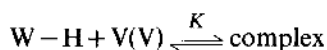
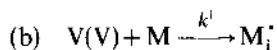
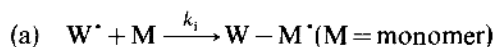


Figure 4. Variation in percentage of grafting at a fixed time. Effects of solvent composition: wool = 0.2 g; [AA] = 1.46 M; $[V^{15}] = 0.015$ M; time = 6 h; temp = 45°C. (○) controlled value = 46.25%; (■) acetone; (□) acetic acid; (○) methanol; (●) formic acid; (●) pyridine; (▲) cyclohexanone.

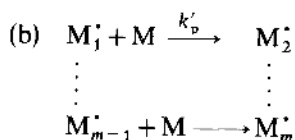
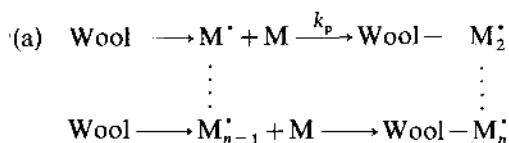
lecular fashion to yield transient free radicals on the wool backbone. These free radicals initiate grafting. The termination of the growing polymer chains is caused by excess of metal ions. Oxidation of the transient free-radicals to products and dimerization of two macro wool radicals have also been suggested.



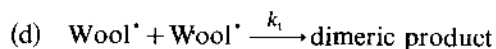
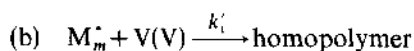
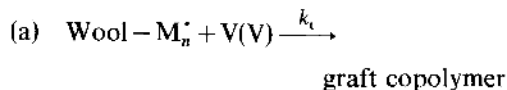
Initiation:



Propagation:



Termination:



Applying the steady state approximation and assuming simple graft copolymerization, the rate of graft copolymerization was derived as follows:

$$R_p = \frac{Kk_p k_i k_r [M]^2 [Wool-H]}{k_t (k_i [M] + k_o [V(V)])}$$

Properties of the Grafts

(1) *Behaviour towards Acids and Alkalis.* Acrylic acid grafted wool fibers showed higher affinity to alkalis in comparison to the ungrafted wool, probably due to the formation of corresponding sodium salts and to some extent due to the solubility of polyacrylic acid chain. Moderate resistance to the action of mineral acids at room temperature was observed. However at elevated temperatures and higher concentrations the grafted samples underwent deterioration and became brittle.

(2) *Tensile strength.* The tensile strength of the polyacrylic acid grafted wool fibers was determined from stiffness at the break following the method of Houque *et al.*⁶⁸ and Samal *et al.*⁶⁹ The stiffness at the break was determined from the tenacity and elongation at the break using the relationship:

$$\text{Stiffness at break} = \frac{\text{Tenacity at break}}{\text{Elongation at break}} \times 100$$

The tenacity was expressed in g/denier. After conditioning the grafted samples, they were combed and fiber aggregates of uniform length were taken, weighed and their lengths determined. Tensile strength was determined by a "Dutrons" Tensile Tester, Brand—20 kfg capacity.

The results in Table II show that the tensile modulus of the wool fibers increases with the percentage of grafting upto 46.2% beyond which it decreases. The enhancement of tensile modulus upto the cited range may be attributed to entanglement of the grafted polyacrylic acid chains thus adding to the elastic behaviour of the fiber. The graft copolymer of percentage of grafting, 62.7%, 90.05%, and

Table II. Effects of percentage of grafting on tensile properties of acrylic acid grafted wool fibers

Samples	Grafting	Elongation at break	Tenacity at break	Tensile modulus
	%	B.L. %	g/denier	
Parent fiber	0	1.48	2.75	185.8
Wool-g-PAA	8.6	1.49	2.78	186.6
	14.3	1.50	2.81	187.3
	36.6	1.52	2.9	190.8
	46.2	1.58	3.2	202.5
	62.7	1.54	3.1	201.3
	90.0	1.39	1.4	100.7
	193.7	0.32	0.54	59.2

193.7% should have contributed more towards the elastic behaviour of the grafted sample but it showed a decrease in tensile modulus and the samples became more and more brittle. The probable explanation for this behaviour may be the reaction conditions under which they were prepared. These samples were prepared at high concentration of V^{+5} , i.e., $15 \times 10^{-3} M$, $20.0 \times 10^{-3} M$, and $25 \times 10^{-3} M$, respectively. At these concentrations of V^{+5} in the reaction mixture, the backbone of the base wool fibers must undergo progressive oxidation and acid hydrolysis with increase in V^{+5} concentration. Due to this oxidative and hydrolytic degradation the graft copolymers (62.7–193.7%) exhibit decreasing tensile modulus.

(3) *Dye Uptake.* Sandocryl Golden yellow B-GRL 300% dye was used for dyeing the fibers. The dye solution was prepared by adding 1 g of dyestuff to 100 ml of hot water with constant stirring to obtain a clear solution. 1% shade was dyed on the material. The required amount (10 ml) of the dye solution was placed in a breaker and to that 4 ml of 1% ammonium sulphate solution were added. The material to liquor ratio was adjusted to 1:40 by adding the required amount of water. The pH of the dye solution was then maintained between 5–5.5 by adding dilute acetic acid dropwise. The concentration of the dye in this solution was

Table III. Effect of percentage of grafting on dye uptake ability of parent wool and acrylic acid grafted wool fibersInitial concentration of the dye solution = 13.23×10^{-4} .

Sample No.	Grafting — %	Absorbance (O.D)	Concentration of the dye after dyeing	Dye uptake in g of the dye g^{-1} of the fiber	Dye uptake in g of the dye kg^{-1} of the fiber
Raw wool	—	0.155	4.75×10^{-4}	8.48×10^{-4}	8.48×10^{-1}
Wool-g-PAA	50%	0.109	3.34×10^{-4}	9.89×10^{-4}	9.89×10^{-1}
Wool-g-PAA-Na-salt	After 50% dyeing it was converted to Na salt	0.600	1.84×10^{-4}	11.39×10^{-4}	11.39×10^{-1}

Table IV. Water retention of the Wool-g-PAA samples at various percentages of grafting

Samples	Percentage of grafting	Water retention in $g g^{-1}$
Parent fiber	0	3.0
Wool-g-PAA	8.6	6.2
	14.3	8.4
	36.6	16.5
	46.2	20.8
	62.7	28.9

measured by a spectrophotometer at 750 nm. The sample was prewetted and dipped into the dye solution. The breaker was then kept over a hot plate and the temperature was raised to $80^{\circ}C$ by $5^{\circ}C \text{ min}^{-1}$, then from $80-100^{\circ}C$ the temperature was raised slowly by $1^{\circ}C \text{ min}^{-1}$. Dyeing was carried out at $100^{\circ}C$ for 45 min till all the colour was gone from the fiber. After dyeing, the material was rinsed in cold water and air dried. The initial concentration of the dye solution and that remaining after dyeing were determined by the following formula

$$C = \frac{\text{O.D.}}{a_{\lambda}}$$

where

O.D. = optical density

a = constant ($0.4343k$)

λ = 750 nm.

The resulting dye uptake ability of the fibers was determined by measuring the difference in

the initial and remaining concentrations of the dye solution and is shown in Table III. The results showed that grafting of acrylic acid increases the dye uptake ability of wool fibers.

(4) *Absorption of Water and Water Vapours (Water Retention)*. The extent of absorption of water and water vapours of both the grafted and virgin wool fibers was determined by measurement of water retention of the samples following the method of Rånby *et al.*⁷⁰ with slight modification. The water retention increased with the percentage of grafting. One gram of both virgin and grafted fibers was separately immersed in 100 ml of distilled water for 12 h. The contents were then filtered through a sintered glass filter and sucked at 700 mmHg pressure. The volume of the filtrate was measured and the water retention equal to the amount of water absorbed was calculated as g of water per g of dry material.

Acknowledgement. The authors are very thankful to Prof. Y. Ikada, Research Centre for Medical Polymers and Biomaterials, Kyoto University, Japan for his continuous inspiration and valuable suggestions.

The financial support by C.S.I.R., India, New Delhi is gratefully acknowledged.

REFERENCES

1. P. Alexander and R. F. Hudson, "Wool. Its Chemistry and Physics," Reinhold, New York, N. Y., 1954, p 334 FF.

2. N. H. Koenig, U. S. Patent 2993748 (July 25, 1961).
3. N. H. Koenig, *Textile Res. J.*, **32**, 117 (1962).
4. H. Fraenkel-Conrat, M. Cooper, and H. S. Olcott, *J. Am. Chem. Soc.*, **67**, 314 (1945).
5. N. H. Koenig, paper presented at the Technical Wool Conference San Francisco, California, May 13, 1964 [*Textile Res. J.*, **35**, 708 (1965)].
6. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *J. Appl. Polym. Sci.*, **8**, 1607 (1964).
7. W. Fong, R. E. Whitfield, L. A. Miller, and A. H. Brown, *Am. Dyestuff. Repr.*, **51**, 325 (1962).
8. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Textile Res. J.*, **31**, 704 (1961).
9. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Textile Res. J.*, **32**, 473 (1962).
10. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Textile Res. J.*, **33**, 440 (1963).
11. L. A. Valentine, *J. Text. Inst.*, **46**, 270 (1965).
12. H. Ishibashi and M. Oku, Proceedings of International Wool and Textile Research Conference, Paris, 1965, Section III, p 385.
13. M. Negishi, K. Arai, and S. Okada, *J. Appl. Polym. Sci.*, **11**, 115 (1967).
14. J. L. Williams and V. Stannett, *Text. Res. J.*, **38**, 000 (1968).
15. H. L. Needles and W. L. Wasley, *Text. Res. J.*, **39**, 97 (1969).
16. I. C. Watt, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C5**, 176 (1970).
17. H. L. Needles, L. J. Sarfield, and D. M. Dawhaniuk, *Text. Res. J.*, **42**, 558 (1972).
18. K. Arai, M. Negishi, S. Komine, and K. Takada, *Appl. Polym. Symp.*, **18**, 545 (1971).
19. H. L. Needles and L. J. Sarfield, *Appl. Polym. Symp.*, **18**, 569 (1971).
20. A. J. Makinnon, *J. Appl. Polym. Sci.*, **14**, 3033 (1970).
21. D. S. Varma and R. K. Sarkar, *Text. Res. J.*, **41**, 610 (1971).
22. A. Hebish and A. Bendak, *Teintex*, **10**, 719 (1971).
23. A. Kantouch, A. Hebeish, and A. Bendak, *Eur. Polym. J.*, **7**, 153 (1971).
24. W. S. Simpson, *Appl. Polym. Symp.*, **18**, 967 (1971).
25. A. Kantouch, S. Abdel-Fattah, and A. Hebeish, *Polym. J.*, **3**, 375 (1972).
26. A. Hebeish, A. Bendak, and S. Abdel-Fattah, *Angew. Makromol. Chem.*, **37**, 11 (1974).
27. S. Abdel-Fattah, A. Kantouch, and A. Hebeish, *Angew. Makromol. Chem.*, **43**, 11 (1975).
28. A. Hebeish, S. H. Abdel-Fattah, and M. H. El. Rafie, *J. Appl. Polym. Sci.*, **20**, 3449 (1976).
29. N. C. Pati, S. Lenka, and P. L. Nayak, *Die Angew. Makromol. Chemie*, **71**, 189 (1978).
30. B. N. Mishra, I. Kaur, and R. K. Sharma, *Polym. Bull. (Berlin)*, **4**, 635 (1981).
31. P. L. Nayak, G. Sahu, and S. Samal, *J. Macromol. Sci. Chem.*, **A16**, 1309 (1981).
32. M. K. Mishra and B. L. Sar, *J. Macromol. Sci. Chem.*, **A18**, 575 (1982).
33. S. Samal, G. Sahu, and P. L. Nayak, *J. Macromol. Sci. Chem.*, **A20**, 153 (1983).
34. J. S. Shukla, G. K. Sharma, R. K. Tewari, and S. K. Shukla, *J. Macromol. Sci. Chem.*, **A21**, 225 (1984).
35. J. S. Shukla and G. K. Sharma, *Indian J. Chem. Sect. A*, **A24**, 467 (1985).
36. J. S. Kim and W. S. Ha, *Han'guk Somyu Konghakhoechi*, **23**, 472 (1986).
37. J. S. Shukla, S. C. Tewari, and G. K. Sharma, *J. Appl. Polym. Sci.*, **34**, 191 (1987).
38. B. O. Bateup, H. D. Feldtman, and B. E. Fleisch-Fresser, *J. Text. Inst.*, **72**, 34 (1981).
39. A. Kantouch, A. Bendak, and M. Sadek, *Text. Res. J.*, **48**, 619 (1978).
40. W. J. Thorsen, *Ozone. Sci. Eng.*, **1**, 219 (1979).
41. J. D. Garcia, P. Erra, A. M. Dela, M. R. Julia, A. Barella, and T. Shaw, *J. Text. Inst.*, **71**, 165 (1980).
42. N. H. Koenig and M. Friedman, U. S. Patent Applied 57858, 15 February 1980, Applied 16 July 1979, p 14.
43. R. J. Cook and E. D. Rivett, *Text. Res. J.*, **57**, 596 (1981).
44. R. L. Greaves, P. H. Roche, and M. A. White, *Text. Res. J.*, **5**, 681 (1981).
45. E. E. Ney, R. Peake, and N. Regos, *Colourage*, **28**, 31 (1981).
46. K. Byrne, Eur. Patent Applied Ep. 209323, 21 January 1987, GB Applied 85/17,740, 13 July 1985, p 11.
47. M. A. Parry, Br. Patent GB Applied 2, 174424, 05 November 1986, GB Applied 85/10,038, 19 April 1985, p 6.
48. B. H. Jang, S. W. Nam, and M. Sakamoto, *Han'guk Somyu Konghakhoechi*, **24**, 68 (1987).
49. P. Erra, M. R. Julia, P. Burgues, and M. R. Infante, *Tenside, Surfactante, Deterg.*, **25**, 275 (1988).
50. P. Erra, M. R. Julia, M. R. Infante, M. L. Coderch, and J. J. G. Dominguez, *J. Soc. Dyers Colour.*, **104**, 93 (1988).
51. A. Szpala, Eur. Patent Applied Ep. 260017, 16 March 1988, GB Applied 86/21,171, 02 September 1986, p 16.
52. R. K. Samal and G. Giri, *J. Macromol. Sci. Rev. Macromol. Chem.* (communicated).
53. W. A. Waters and J. S. Littler, "Oxidation in Organic Chemistry," Part-A, K. B. Wiberg, Ed., Academic Press Inc., New York, 1965, pp 186-240.
54. Y. Ikada, Y. Nishizaki, Y. Uyama, T. Kawahara, and I. Sakurada, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2251 (1976).
55. S. F. Sadova, M. V. Korchagin, and E. O. Kazakova, *Otkrytiya, Izobret., Prom. Obraztsy. Tovarnye Znuki*, **54**, 107 (1977).
56. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **71**, 189 (1978).

Graft Copolymerization of Acrylic Acid onto Wool Fibers

57. P. L. Nayak, S. Lenka, and N. C. Pati, *J. Appl. Polym. Sci.*, **22**, 3301 (1978).
58. G. Wu, D. Lu, P. Zhou, J. He, and W. Tao, *Jilin Daxue Ziran Kexue Xuebao*, No. 2, 77 (1983).
59. N. G. Gaylord, *J. Polym. Sci., C*, **37**, 153 (1972).
60. A. Hebeish, M. I. Khalil, and M. H. El-Rafie, *Angew. Makromol. Chem.*, **37**, 149 (1979).
61. R. K. Samal, P. K. Sahoo, and H. S. Samantaray, *J. Appl. Polym. Sci.*, **32**, 5693 (1986).
62. R. K. Samal, P. L. Nayak, and M. C. Nayak, *Die. Angew. Macromol. Chem.*, **80**, 95 (1979).
63. R. K. Samal, S. C. Satrusallya, B. L. Nayak, and C. N. Nanda, *J. Appl. Polym. Sci.*, **28**, 1311 (1983).
64. W. Kern, R. Schulz, G. Renner, and A. Henglein, *Makromol. Chem.*, **12**, 20 (1954).
65. S. R. Palit and R. S. Konar, *J. Ind. Chem. Soc.*, **38**, 481 (1961).
66. R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, **25**, 1901 (1970).
67. M. Kinoshita, Y. Miura, and S. Masuda, *Makromol. Chem.*, **160**, 243 (1972).
68. M. M. Haque and M. D. Habibuddin, *Bangladesh J. Sci. Ind. Res.*, **15**(1-4), 64 (1980).
69. R. K. Samal, H. S. Samantaray, and R. N. Samal, *Polym. J.*, **18**, 471 (1986).
70. B. Ranby and L. Gadda, *Am. Chem. Soc. Symp. Ser.*, **187**, 33 (1982).