Characterization of Wool Graft Copolymers

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Synopsis

In the present article, characterization of wool grafted with acrylate monomers such as methyl methacrylate (MMA), methylacrylate (MA), ethylacrylate (EA), and butylacrylate (BA) with respect to thermal behavior and viscosity average molecular weight ($\overline{M}_v$) is described. The modified wool shows improved thermal behavior.

INTRODUCTION

Wool graft copolymers have been successfully prepared by treatment of wool samples with vinyl monomers in the presence of a variety of initiator systems by different groups of workers.[1-3] We have prepared a large number of wool grafts using redox systems,[4,5] radical initiators,[6] metal chelates,[7] and gamma rays[8,9] as initiators. In the present article an attempt has been made to characterize graft copolymers of wool prepared in our laboratory by studying the thermal behavior. $\overline{M}_v$ of the homopolymer isolated from the grafts has also been determined as a function of graft level.

Thermal behavior of wool and chemically modified wool has been studied by Sadhir and his co-workers.[10] A comparison of temperatures for different percentage decomposition reveals that thermal stability of wool fiber decreases significantly after chemical treatment with thioglycollic acid. Varma and Sadhir[11] prepared wool grafts of PMMA using the γ-irradiation method. They studied the thermal behavior of the modified wool and natural wool and reported that the modification by oxidation, alkylation, and graft copolymerization affects the thermal behavior of the wool fiber. Thermogravimetric studies of natural and flame retardant wool have been reported by Beck and Gordon.[12] Small changes above 200°C in differential thermograms of wool fibers grafted with vinyl monomers were reported by Needles.[13] Thermogravimetric and differential thermogravimetric analysis of natural wool and chemically modified wool have been reported by Schwenker et al.[14]

Various groups of workers have attempted isolation of the grafted polymers from the wool grafts in order subsequently to determine the viscosity average molecular weights of the grafted polymer as a function of graft levels and the nature of the initialing systems employed for effecting graft copolymerization. Negeshi et al.[15] have used 72% sulfuric acid digestion method to separate grafted polymers from the wool trunks. They also hydrolyzed grafted wool with 6N HCl for 24 h at 115°C.[2] From the weight decrease of the starting material it was found that wool completely decomposed without the loss of grafted polymers. Campbell and co-workers[16] have shown that about one half

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of the styrene-grafted chains isolated by hydrolysis of grafted wool samples with sodium hydroxide was soluble only in such solvents as DMF and benzene–methanol mixtures. The lack of benzene solubility of polymer was caused by the presence of some amino acid residues.

Arai and co-workers[17] have used the two-step HCl digestion method to isolate grafted polymer of wool and chemically modified wool. They showed that few amino acid residues were left in the end of the polymer chain. Treatment of grafted wool with cold aqueous sodium hypochlorite solution was investigated by Stannett et al.[18] who separated polystyrene from grafted wool, prepared in methanol–dioxane mixture by treatment with a mixture of benzene and 5% potassium hydroxide in 1:1 ratio for about 12 h. Grafted wool forms opaque emulsion. The emulsion was acidified with concentrated HCl and poured into absolute alcohol, and insoluble precipitates were obtained. It was found that the residue could be divided roughly into two equal parts by benzene. The benzene insoluble part was soluble in DMF. The intrinsic viscosity of two fractions were determined in DMF and toluene, respectively.

EXPERIMENTAL

The procedure for the preparation of wool grafts is described in detail elsewhere.[4,5,7]

Thermogravimetric Analysis

Thermal degradation was carried out in air using a Stanton Model HT-D thermogravimetric analyzer. The fiber sample was cut in small pieces and sieved to a size of 30 mesh; 15 ± 1 mg sample was used. Heating rate of 10°C/min was used to heat the sample from room temperature to 725°C. Primary thermograms were obtained by plotting the percent residual weight against temperature.

The grafted wool samples were prepared by using different initiator systems. The details of the samples used in the present study are given in Table I.

TABLE I

Sample	Initiator system	% Grafting
Wool-*g*-PMMA[22]	FAS–TBHP	145.6
		119.0
		84.1
Wool-*g*-PMA[23]	VO(acac)$_2$	28.4
		17.3
Wool-*g*-PEA[23]	VO(acac)$_2$	18.5
		17.8
Wool-*g*-PEA[24]	Mn(acac)$_3$	28.5
		26.0
Wool-*g*-PBA[24]	Mn(acac)$_3$	26.0

TABLE II
Molecular Weight of the Polymer (PMMA, PMA, and PEA) Isolated
from the Graft as a Function of Percentage of Grafting

Sample no.	Grafted sample	Polymer isolated	% Grafting	$\overline{M}_v$
1	Wool-g-PMA[22]	PMA	25.4	18,410
2			37.5	43,210
3			48.1	53,250
4			56.0	61,240
5	Wool-g-PMMA	PMMA	100.5[22]	92,390
6			102.0[25]	94,160
7			108.0[22]	102,500
8			109.0[25]	126,400
9			111.5[25]	142,300
10	Wool-g-PEA[26]	PEA	28.0	46,560
11			38.5	75,160

Viscosity Average Molecular Weight of Grafted Polymer

Grafted wool samples were hydrolyzed with 1 : 1 mixture of benzene–sodium hydroxide. All the wool goes into solution. The presence of benzene in the hydrolyzing mixture solubilizes the polymer and thus assists in the removal of grafted polymer from the backbone polymer. The $\overline{M}_v$ of polymers isolated from the graft was determined by the viscosity method using a Ubbelohde viscometer and was calculated by using the Mark–Houwink equation:

$$[\eta] = KM^\alpha$$

where K and α are constant for particular solvent at particular reaction conditions. The values of K and α are obtained from the *Polymer Handbook*.[19] $\overline{M}_v$ of different polymers isolated from the graft are presented in Table II.

RESULTS AND DISCUSSION

The extent of grafting may be influenced by the availability of active sites in the polymer backbone. Other variables which influence grafting include concentration of initiator and monomer, time, and temperature. The effects of these parameters on graft copolymerization of a variety of vinyl monomers onto wool has been extensively studied and discussed.[3-9]

Figures 1–4 represent the primary thermograms of wool and grafted wool as a function of percentage of grafting. Figure 1 illustrates the thermograms of wool and wool-g-PMMA as a function of percentage of grafting. Three different stages of decomposition have been identified from the thermogram. The first region shows the inflexions due to moisture. In the primary thermograms of unmodified wool this region lies between 150 and 250°C, whereas in wool-g-PMMA this region shows very small inflexion and this may indicate that grafting reduces moisture absorption. The second stage of decomposition begins at 251°C with 20% weight loss. After that the decomposition continues at a constant rate and reaches a stage where final decomposition starts. The final decomposition temperature (FDT) of wool is 520°C with 85% weight loss.
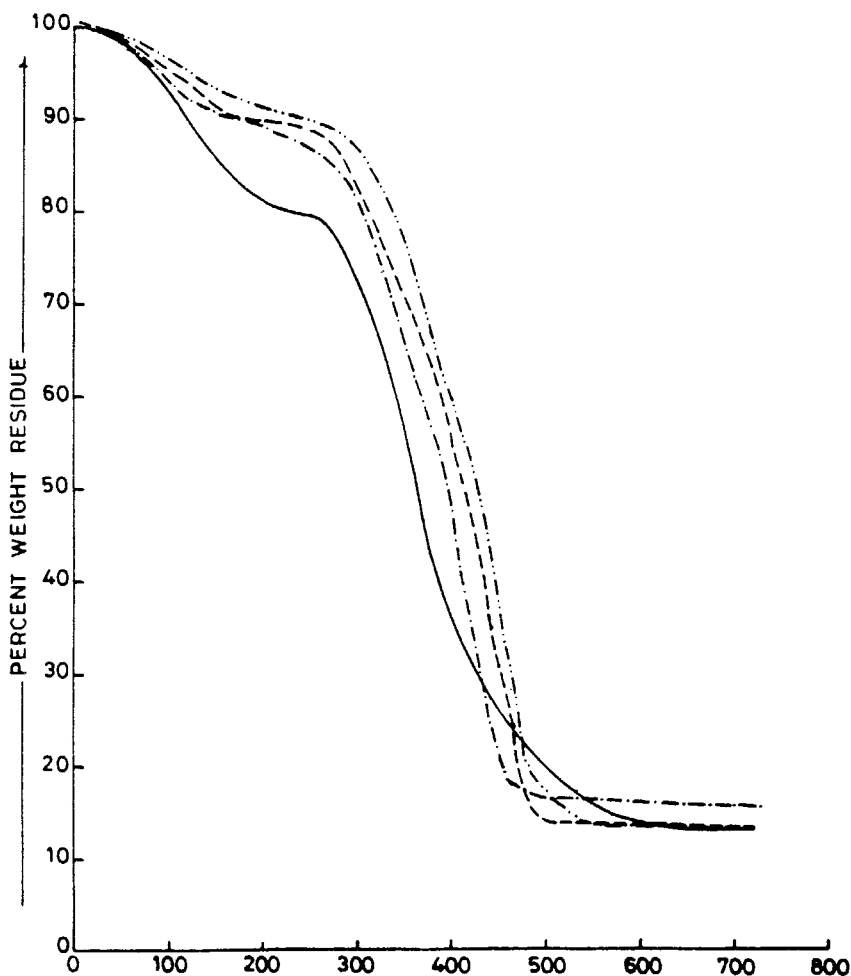
Fig. 1. Primary thermograms of pure wool and wool-g-PMMA: (—) pure wool; (---) 84.10% grafting; (– · –) 119.00% grafting; (– · · –) 145.60% grafting.

Upon further heating up to 725°C, rapid decomposition occurs, and the residue left at 725°C is 15% only.

The initial decomposition temperature of wool-g-PMMA starts at 260°C, the FDT (510°C) lies close to that of wool (520°C). The residue left at 725°C in ·grafted wool is 22%. The initial decomposition temperature (IDT), final decomposition temperature (FDT), and the decomposition temperature (DT) of wool and wool-g-PMMA at different weight loss are presented in Table V. On comparison of thermal data of ungrafted wool and PMMA grafted wool, it is observed that there is an improvement in thermal behavior of the modified wool. It is observed from Table V that IDT, FDT, and DT values of grafted wool increase with increase in percentage of grafting. This increase may be due to the fact that, with addition of polymer chain to the wool backbone, thermal behavior of the wool is changed. The same behavior has also been observed by Bajaj et al.[9] during their studies on thermogravimetric analysis of wool and chemically modified wool. When DT values of wool are compared with those of grafted wool, it is observed that the difference in DT is quite
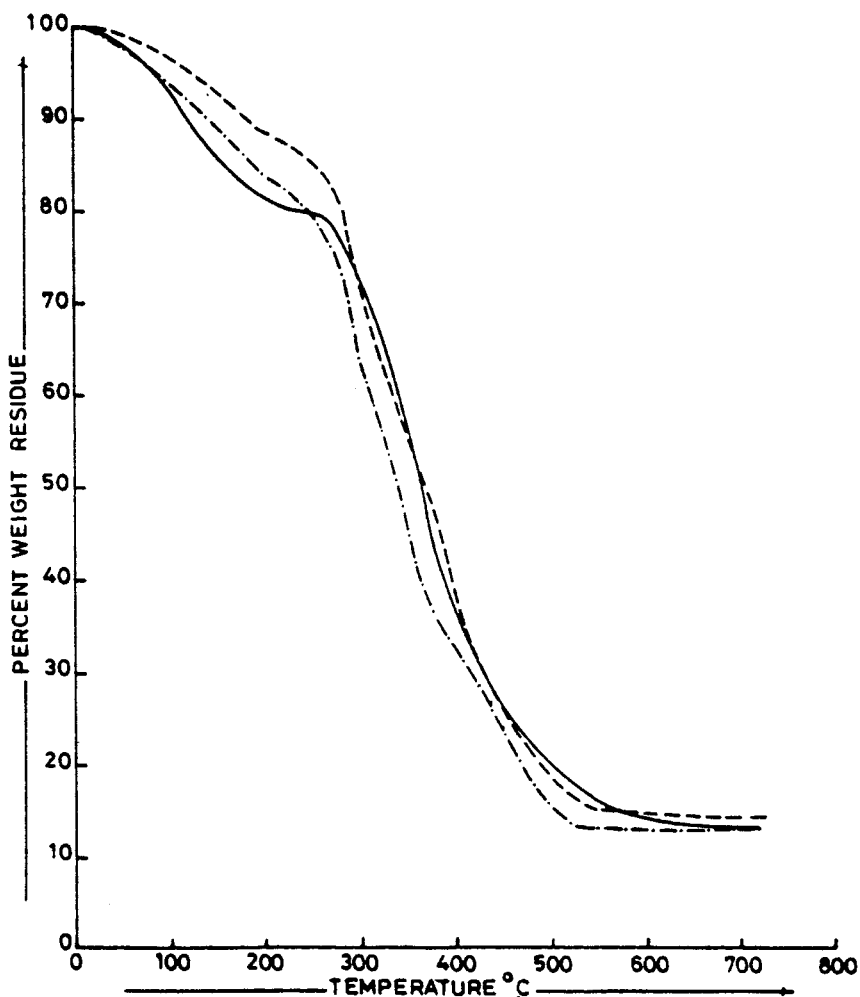
Fig. 2. Primary thermograms of pure wool and wool-*g*-PMA: (—) pure wool; (---) 17.40% grafting; (-·-) 28.40% grafting.

high for every 10% weight loss of the grafted sample, indicating that grafting considerably improves thermal-behavior of wool. Varma and Sarkar[20] studied the thermal properties of wool-*g*-PMMA using dynamic thermogravimetry. They observed three distinct regions of weight loss in the thermograms of wool and grafted wool as discussed above. The thermal stability of wool was found to increase with chemical modification.

Figure 2 represents the primary thermograms of wool-*g*-PMA as a function of percentage of grafting a small inflexion in the primary thermogram indicates small absorption of moisture by the grafted samples. It is observed that the grafted wool with low percentage of grafting (17.4%) shows better thermal behavior than the sample with higher percentage of grafting (28.4%). In the former case the second decomposition stage starts at 275°C (IDT) with 16% weight loss and the third stage begins at 545°C with 85% weight loss. When the temperature is further raised to 725°C, the residue left is 14%. The DT values at various weight losses are presented in Table V.
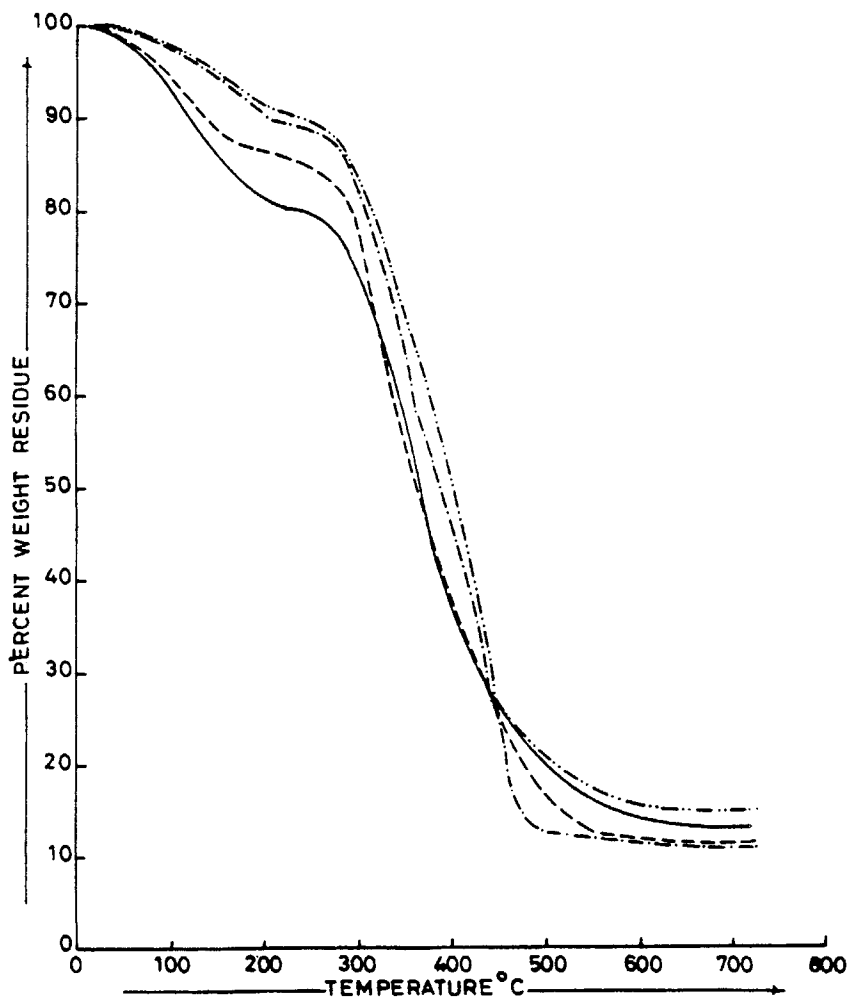
Fig. 3. Primary thermograms of pure wool and wool-*g*-PEA: (—) pure wool; (---) 18.50% grafting; (-·-) 26.00% grafting; (-··-) 28.50% grafting.

On comparison of the thermal behavior of wool and wool-*g*-PMA, it is observed that not much difference exists in DT values of wool and wool-*g*-PMA but the IDT and FDT values of grafted wool (wool-*g*-PMA) are much higher .than those of wool, indicating that grafting of PMA chains onto wool produces small improvement in the thermal behavior of wool.

Primary thermograms of wool-*g*-PEA, presented in Figure 3, describes the thermal behavior of wool grafted with PEA as a function of percentage of grafting. It is observed that with increase in percentage of grafting, the IDT value decreases. The same behavior is observed in case of wool-*g*-PMA (Fig. 2). Our results are in agreement with those reported by Varma and Sarkar,[21] who observed that wool grafted with EA and MA showed higher thermal stability at lower graft add-on and poorer thermal stability with increasing percentage of grafting. The third stage of decomposition starts at 585°C, which is higher than the FDT of wool (520°C). The residue left at 725°C is 10–20%. The IDT, FDT, and DT values at different weight losses are presented in Table V.
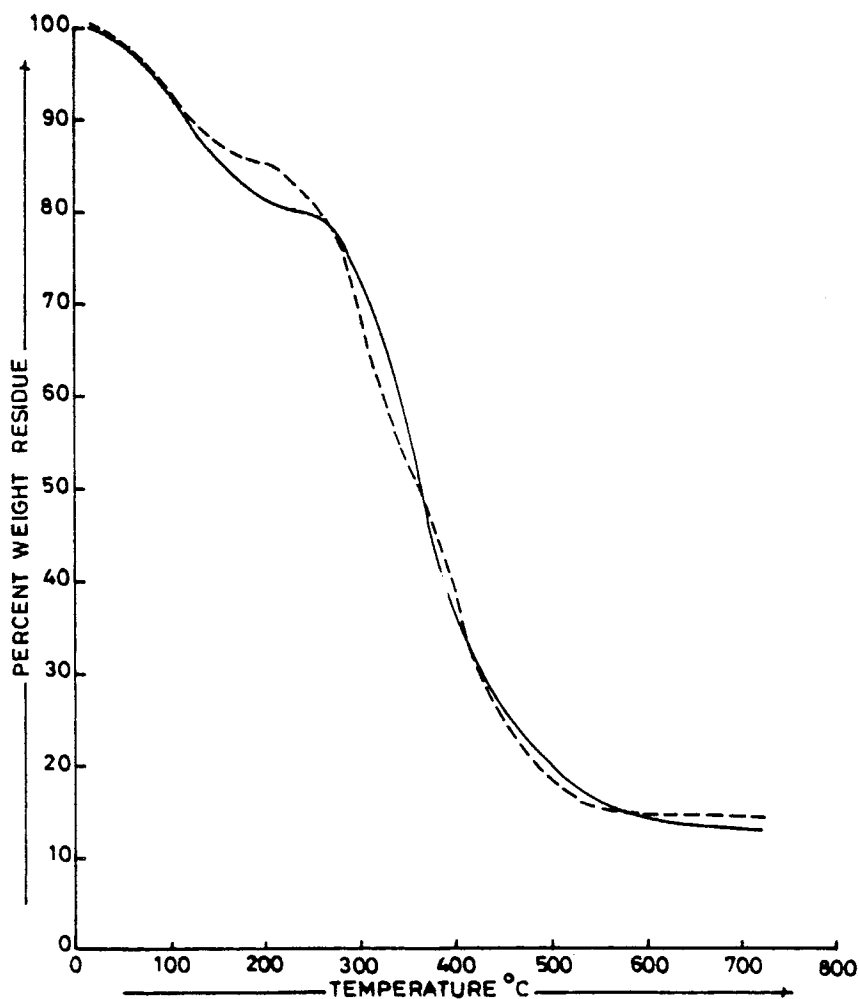
Fig. 4. Primary thermograms of pure wool and wool-*g*-PBA: (—) pure wool; (---) 26.00% grafting.

TABLE III
Molecular Weight of Polymer (PMA and PEA) as a Function
of Initiator Concentration [TBHP]

Sample no.	Grafted sample	Polymer isolated	[TBHP] $\times 10^2$ (mol/L)	$\overline{M}_v$
1	Wool-*g*-PMA[26]	PMA	10.0	106,500
2		PMA	15.0	96,160
3	Wool-*g*-PEA[26]	PEA	5.0	79,110
4		PEA	10.0	117,500

TABLE IV
M_v of PEA, PBA, and PMMA Isolated from the Graft
as a Function of Monomer Concentration

Sample no.	Grafted sample	Polymer isolated	$[M] \times 10^2$ (mol/L)	$\overline{M}_v$
1	Wool-g-PEA[24]	PEA	41.4	48,140
2			50.6	59,910
3	Wool-g-PBA[24]	PBA	17.5	16,210
4			31.6	59,920
5			38.6	55,750
6	Wool-g-PMMA[22]	PMMA	14.1	40,980
7	Wool-g-PMMA[22]		23.5	107,600
8			32.9	145,100

TABLE V
Initial Decomposition Temperature (IDT), Final Decomposition Temperature (FDT),
and Decomposition Temperature (DT) for Every 10% Weight Loss
of Wool and Grafted Wool Samples

Sample no.	Sample	% Grafting	Initiator	IDT (°C)	FDT (°C)	DT (°C) for every 10 wt% loss							
						10%	20%	30%	40%	50%	60%	70%	80%
1	Wool	—	—	251	528	120	240	310	345	365	385	427	500
2	Wool-g-PMMA	84.1	FAS–TBHP	270	485	175	315	355	390	415	435	455	470
3		119.0		285	470	180	305	340	370	400	415	435	455
4		145.6		310	510	260	340	375	400	430	450	465	480
5	Wool-g-PMA	17.4	VO(acac)$_2$	275	545	180	280	310	340	370	400	430	490
6		28.4		280	520	140	250	290	310	340	370	420	470
7	Wool-g-PEA	18.5	VO(acac)$_2$	295	585	130	270	315	335	360	390	430	475
8		23.0	Mn(acac)$_3$	280	550	200	305	335	355	385	415	435	510
9		28.5		275	475	240	315	345	375	400	425	440	460
10	Wool-g-PBA	23	Mn(acac)$_2$	265	535	120	265	295	325	365	400	425	500

Figure 4 describes the primary thermogram of wool-g-PBA with 23% grafting. The IDT, FDT, and also the DT values almost lie in the same range as that of unmodified wool. This suggests that wool grafted with poly(butyl acrylate) does not show improvement in thermal behavior.

From the foregoing discussion, it is observed that grafting of PMMA, PMA, and PEA onto wool improves the thermal stability of the wool. Vinyl monomers differ in their ability to impart thermal stability to the grafts, and the following thermal stability order for different grafted samples was observed:

wool-g-PMMA > wool-g-PMA > wool-g-PEA > wool-g-PBA

The above thermal stability order indicates that the monomer which produces maximum percentage of grafting also induces higher thermal stability to the graft. Poly(methyl methacrylate) (PMMA) possesses higher crystallinity which is reflected in its higher T_m (200°C), and it seems that stiffer PMMA chains with lower T_g value (105°C) perhaps are responsible for imparting higher stability. PBA does not significantly improve thermal stability of wool-g-PBA and this may be explained by the fact that polybutylacry-

late polymer does not have significant crystallinity as shown by its low T_m value (47°C).

Isolation of grafted polymer by acid hydrolysis with $6N$ HCl at 115°C afforded a grafted polymer which was partially depolymerized.[2] In the present work all acrylate polymers were isolated from the grafted wool by following the method of Stannett et al.[18]

Tables II–IV describe the viscosity average molecular weights of the polymers isolated from the grafted samples as a function of percentage of grafting and concentration of monomer and initiator. It is observed from Table II that, as the percentage of grafting increases, $\overline{M}_v$ of homopolymers isolated from the grafts also increases. This may indicate that the frequency of grafting is less and longer polymeric chains are attached to the backbone polymer. This may suggest that growing polymeric chains prefer to undergo vinyl polymerization on a particular active site rather than creating additional active sites on wool. This would be expected since creation of additional active sites on wool by abstraction of reaction requires higher energy of activation.

The $\overline{M}_v$'s of PMA and PEA isolated from the grafts were determined as a function of initiator concentration [TBHP], and it is observed that there exists an optimum [TBHP] at which $\overline{M}_v$ of grafted polymer is maximum (Table III). Further increase in [TBHP] decreases $\overline{M}_v$ of both PMA and PEA isolated from the graft. This indicates that at higher [TBHP] termination of growing grafted chains becomes predominant.

Viscosity average molecular weight ($\overline{M}_v$) of PEA, PBA, and PMMA polymers isolated from the grafts as a function of concentration of the monomer are presented in Table III. It is observed that $\overline{M}_v$ increases with increase in monomer concentration. Increase in $\overline{M}_v$ with increasing [M] may indicate that, under the conditions of grafting, polymeric chains are preferentially attached to smaller number of active sites on wool backbone.

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