Polymerization of Allyl Methacrylate with Wool Fabric Using Different Initiators

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Synopsis

Polymerization of allyl methacrylate (AMA) with wool fabrics using different initiators, namely, potassium persulphate, Fe^{2+}—H_2O_2, benzoyl peroxide, ceric ammonium nitrate, and vanadium pentanitrate, was investigated. The percent of polymer add-on depends upon the type and concentration of the initiator. Addition of metallic salts such as Fe^{3+} to the polymerization system enhances polymerization significantly when benzoyl peroxide and potassium persulphate are used independently as initiator. The opposite holds true for ceric ammonium nitrate and vanadium pentanitrate. With Fe^{2+}—H_2O_2, on the other hand, the enhancement is marginal. Also studied was the incorporation of Li^+, Cu^{++}, and Fe^{3+} at different concentrations in AMA—wool–benzoyl peroxide polymerization systems. Determination of the polymer add-on on the basis of double bond analysis revealed that the remained double bond is governed by the magnitude of the polymer add-on as well as by the type of initiator.

INTRODUCTION

Polymerization of vinyl monomers onto wool can be initiated through the formation of free radicals on wool backbone. Such polymerization most probably involves grafting of the vinyl polymers onto wool and/or internal deposition of the vinyl polymer in the interior of the fiber. Irradiation methods as well as chemical methods have been used for inducing vinyl grafting onto and deposits of ungrafted polymer in wool.[1-4] Formation of radicals which are capable of initiating polymerization could be achieved by irradiation of wool by high-energy radiation,[4-7] or low energy radiation in the presence and absence of sensitizers.[8-13] Radicals are also formed when wool is present in a polymerization medium containing a redox system,[14-18] ceric ions,[19-23] Ce^{IV}—amine,[24-26] periodate,[27] potassium persulphate/LiBr,[28] potassium permanganate,[29,30] acetonylacetonato—Cu^{II}—trichloroacetic acid complexes,[31-34] benzoyl peroxide,[35] or azobisisobutyronitrile.[36] Dimethylaniline has been used as a catalyst with cupric nitrate,[37] benzoylperoxide,[38] or benzyl chloride[39] for polymerization of vinyl monomers. To the authors' knowledge, no work has been published yet on polymerization of allyl methacrylate with wool.

It is the aim of this work to study the polymerization of allyl methacrylate with wool using different initiators, namely, benzoyl peroxide (BP), H_2O_2/Fe^{II}, potassium persulphate, pentavalent vanadium (V^V) and ceric ammonium nitrate (CAN). In addition, stability of the allyl double bond of poly(allyl methacrylate) containing wool is examined.

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EXPERIMENTAL

Material

Wool fabric (400 g/m^2, yarn count 23/2 tex for both warp and weft) was supplied by Misr Company for spinning and weaving, Mehala El Kobra, Egypt. The fabric was soxhlet extracted with methanol and air dried at room temperature before use.

Initiators

Benzoyl peroxide (BP), potassium persulphate, ceric ammonium nitrate (Ce^{IV}), vanadium pentanitrate (V^V), H$_2$O$_2$, ferrous sulphate were AR (BDH) grade. Cupric sulphate, ferric sulphate, and lithium chloride were of laboratory grade. Allyl methacrylate (AMA) Merck was freshly distilled before use.

Polymerization Using Ce^{IV}, V^V, Persulphate, or BP

Unless otherwise stated, the polymerization was carried out as follows: 49 mL of solution containing the necessary amount of initiator were introduced into a 100-mL Erlenmeyer flask, and kept in a thermostat for 10–15 min at the specified temperature. The wool sample (0.5 g) and 1 mL of AMA were then introduced in the flask. The flask was well stoppered and the contents stirred occasionally during polymerization. The latter was allowed to proceed for the desired length of time.

Polymerization Using Fe^{++}/H$_2$O$_2$ Redox System

The wool sample (0.5 g) was immersed in a solution containing 10 g/L ferrous ammonium sulphate for 1 h with occasional stirring. After the mentioned time, the wool sample was washed several times with distilled water and then pressed between two filter papers. 48 mL of distilled water were introduced into a 100-mL Erlenmeyer flask, and kept in a thermostate for 10–15 min at the specified temperature. The Fe^{++}-treated wool sample, 1 mL AMA, and 1 mL solution containing the necessary amount of H$_2$O$_2$ were then introduced in the flask. The flask was well stoppered and the contents stirred occasionally during polymerization. After the desired reaction time, the sample was washed well by extraction with several portions of water, with a little soap, followed by soaking several times in ethanol, and then dried. The dried samples were then repeatedly soxhlet-extracted with tetrahydrofuran till constant weight. The increase in weight of the extracted sample, as compared with that of untreated wool sample, was recorded as polymer add-on. The allyl content was measured by bromination.[40]

RESULTS AND DISCUSSION

The ability of various initiators, namely, ceric ammonium nitrate, vanadium pentanitrate, potassium persulphate, H$_2$O$_2$/Fe^{++}, and benzoyl peroxide, at
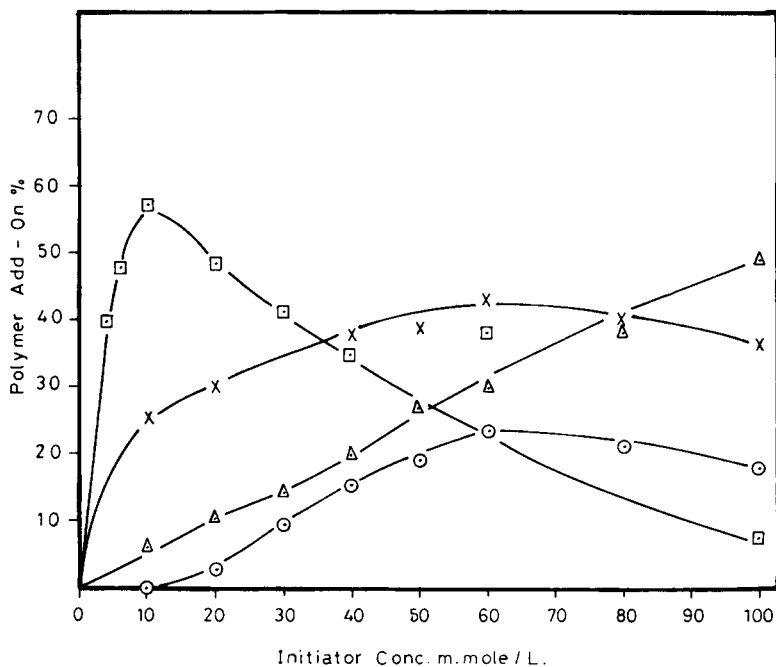
Fig. 1. Variation of the percent polymer add-on with initiator concentration. [AMA], 147.4 mmol/L; material to liquor ratio, 1:100. (—⊙—) Ceric ammonium nitrate (temp, 50°C; time, 2 h); (—△—) vanadium pentanitrate (temp 60°C; time, 4 h); (—✕—) potassium persulphate (temp 60°C; time, 2 h); (▢) Fe^{2+}/H_2O_2 (temp 95°C; time, 2 h).

different concentrations to induce polymerization of allyl methacrylate (AMA) with wool are shown in Figures 1 and 2. The polymerization reactions were carried out using AMA at a concentration of 147.4 mmol/L and a material to liquor ratio of 1:100 for 2–4 h at temperatures that have been reported[18,19,28,35] as optimal for polymerization using these initiators.

It is seen (Figs. 1 and 2) that the polymer add-on increases significantly as the concentration of either H_2O_2 or BP increases to attain a maximum and then decreases sharply by further increase in concentration. However, the magnitude of polymer add-on found with H_2O_2 is far greater than that for benzoyl peroxide. Moreover, maximum polymer add-on is obtained at H_2O_2 concentration of 10 mmol/L, while BP concentration of 2 mmol/L constitutes the optimal concentration for maximum polymer add-on.

That there are optimal concentrations of the peroxides to achieve maximum percent polymer add-on calls for fast rate of initiation of polymerization at relatively low peroxide concentration and fast termination at relatively high peroxide concentration (Figs. 1 and 2). This is rather in conformation with previous reports.[41,42]

Figure 1 shows that the percent of polymer add-on increases by increasing the persulphate concentration up to 60 mmol/L and then tends to decrease by further increase in persulphate concentration. The same holds true for Ce^{IV}. With V^V, on the other hand, the percent polymer add-on increases within the range studied (i.e., 10–100 mmol/L). This reflects the difference in mode of interaction be-
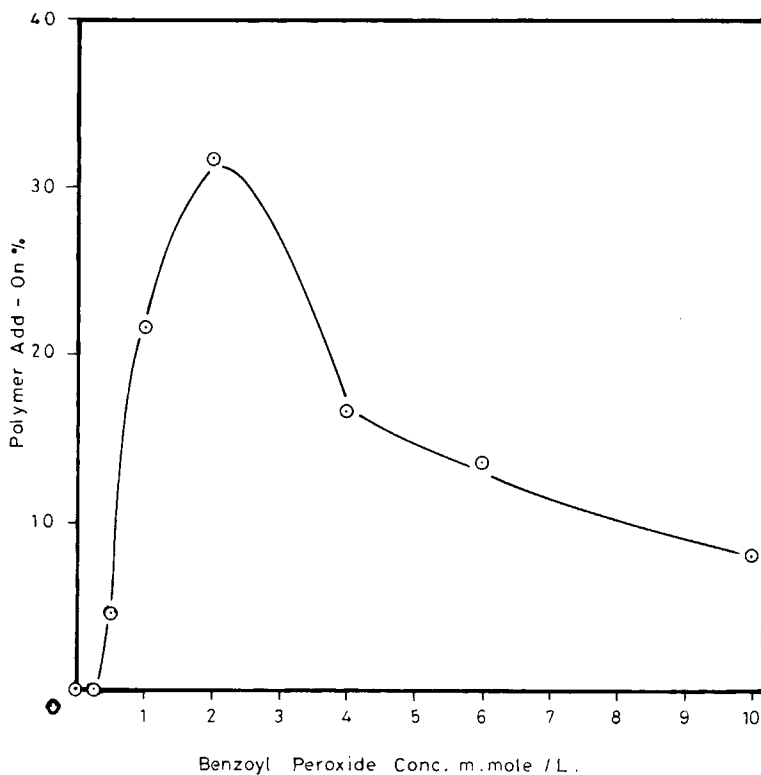
Fig. 2. Variation of the percent polymer add-on with benzoyl peroxide concentration. [AMA], 147.4 mmol/L; temp, 75°C; time, 2 h; material to liquor ratio, 1:100.

tween the initiator and wool which, in turn, are reflected on the percent polymer add-on. Initiation of AMA polymerization by persulphate perhaps occurs via formation of wool radical resulting from the attack of SO_4^- and/or $\cdot OH$ radicals on wool.[43] On the other hand, initiation of polymerization by Ce^{IV} or V^V proceeds via complexation with wool and dissociation of this complex to produce wool radical capable of initiating polymerization.[19,20]

A point of interest is that, although the mode of interaction of Ce^{IV} and V^V with wool is similar, the trend observed with the effect of their concentrations on the percent polymer add-on is different. This indicates that the mode of interaction of the initiator with the wool is not the only deciding factor in polymerization of AMA with wool. Other factors such as affinity of wool to the initiator and their ability for complexation, ease of dissociation of the said complex, efficiency of the wool radical formed as a result of this dissociation, and contribution of the initiator (Ce^{IV} or V^V) in termination have to be exercised.

If the percent polymer add-on obtained with the various initiators used are compared at their most favorable concentrations, Fe^{++}/H_2O_2 would appear as the most effective initiator while the Ce^{IV} is the least. The percent polymer add-on follows the order

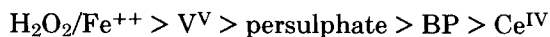$$H_2O_2/Fe^{++} > V^V > \text{persulphate} > BP > Ce^{IV}$$

TABLE I
Effect of Metallic Ion Concentration on Percent Polymer Add-on Using BP as Initiator

Cation concn (mmol/L)	Polymer add-on %		
	Li^+	Cu^{++}	Fe^{+++}
0	11	11	11
0.5	13.6	18.4	39.5
1.0	16	32.8	43.6
2.0	18	41.1	58.4
5.0	18	50	67.2
10.0	18	55	68.6
15.0	18	55	69.8

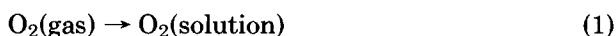65°C; time, 45 min; BP, 2 mmol/L; material to liquor ratio, 1:100; 147.4 mmol/L AMA.

Addition of Metallic Ions

Previous studies have shown that the presence of metallic ions such as Cu^{++} and Fe^{+++} ions during free radical graft polymerization of vinyl monomers onto cellulose,[44-46] wool,[47] nylon,[48] and poly(ethylene terephthalate) fibers[41] enhances grafting significantly. It therefore appears of interest to establish the influence of such ions on polymerization of AMA with wool under the initiating action of BP.

Table I shows the effect of incorporation of Li^+, Cu^{++}, and Fe^{+++} ions at different concentrations on the percent polymer add-on. Obviously, presence of the cation in the polymerization system causes a significant enhancement in the percent polymer add-on. This enhancement depends upon the concentration and type of the cation. There is an increase in the percent polymer add-on by increasing the cation concentration up to a certain limit (depending upon the type of cation) beyond which the cation concentration has practically no effect on the percent polymer add-on within the range studied. Of the cation used, the Fe^{+++} ion exerts the most favorable effect on the percent polymer add-on. Based on the polymer add-on, the following order may be drawn: $Fe^{+++} > Cu^{++} > Li^+$.

The greater efficiency of Fe^{+++} ions in producing higher polymer add-ons than both Cu^{++} and Li^+ ions could be associated with differences in mode of adsorption on the wool. Previous reports[49,50] on the adsorption of several metallic ions with silk, wool, cellulose, and poly(vinyl chloride) have shown ionic and chelate bond formation, depending upon the type of metallic ion used. It seems that Li^+ and Cu^{++} ions are strongly associated with wool, perhaps through ionic and chelate bonding, as compared with the Fe^{+++} ion. As a result, the contribution of the latter in polymerization reaction would be more pronounced than Li^+ and Cu^{++} ions. In any event, however, the significant enhancement in percent polymer add-on by the presence of the cation, e.g., the Cu^{++} ion, can be ascribed to a variety of reasons. First, the Cu^{++} ion accelerates the decomposition of BP. Decomposition of peroxides by metallic ions is well established.[51,52] Second, AMA and Cu^{++} ions forms perhaps a redox system. As a result, Cu^{++} is converted to Cu^+. Third, the cuprous ion would be oxidized back to cupric state by atmospheric (and occluded) oxygen, and this conversion must presumably entail radical intermediate as shown in the following[48,49]:

$$O_2(gas) \rightarrow O_2(solution) \quad (1)$$

$$O_2 + Cu^+ \rightarrow CuO_2^+ \quad (2)$$

$$CuO_2^+ + H^+ \rightarrow Cu^{++} + HO_2^{\cdot} \quad (3)$$

The HO_2 radical may be involved presumably in the initiation of polymerization of AMA with wool or can undergo a reaction leading to formation of hydrogen peroxide as well as hydroxyl radical. Furthermore, the formation of both the $HO\cdot$ and HO_2 radicals in the decomposition of hydrogen peroxide by metallic ion has been reported.[51,52]

The outstanding enhancement in the percent polymer add-on by incorporation of the Fe^{+++} ion in the polymerization system evoked our interest for further studies. Figures 3 and 4 show the rate of polymerization of AMA with wool in the absence and presence of Fe^{+++} using different initiators. Polymerization was carried out at the most favorable temperature and concentration for each initiator in presence of Fe^{+++} (5 mmol/L). It is seen that the favorable effect of the Fe^{+++} ion on the percent polymer add-on is only significant when either BP or persulphate was used as initiator.

Unlike BP and persulphate, the presence of Fe^{+++} in the polymerization induced by Ce^{IV} or V^V ion decreases the percent polymer add-on, particularly during the latter stages of the reaction. This suggests: (a) that presence of Fe^{+++} impedes complexation of Ce^{IV} or V^V with wool; or (b) that the Fe^{+++} ion adversely affects dissociation of the Ce^{IV} or V^V or (c) that the Fe^{+++} ion participates largely in termination of the growing polymer chain and/or wool radical. With the Fe^{++}/H_2O_2 redox system, on the other hand, addition of the Fe^{+++} ion has marginal effect on the rate of polymerization of AMA with wool.

Fig. 3. Rates of polymerization of AMA with wool using different initiators. [AMA], 147.4 mmol/L; material to liquor ratio, 1:100. (——) In absence of Fe^{3+} ion; (------), in presence of Fe^{3+} ion, ferric sulphate concentration, 5 mmol/L; (—⊙—) ceric ammonium nitrate (concn, 40 mmol/L; temp, 60°C) (—▲—) vanadium pentanitrate (concn, 75 mmol/L; temp, 60°C) (—X—) potassium persulphate (concn, 30 mmol/L; temp, 60°C); (—☐—) Fe^{2+}/H_2O_2 (concn of H_2O_2, 10 mmol/L; temp, 95°C).
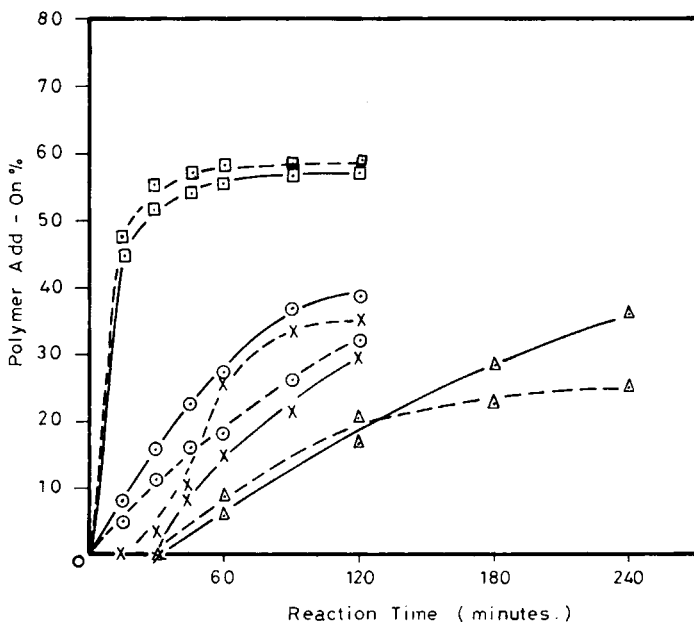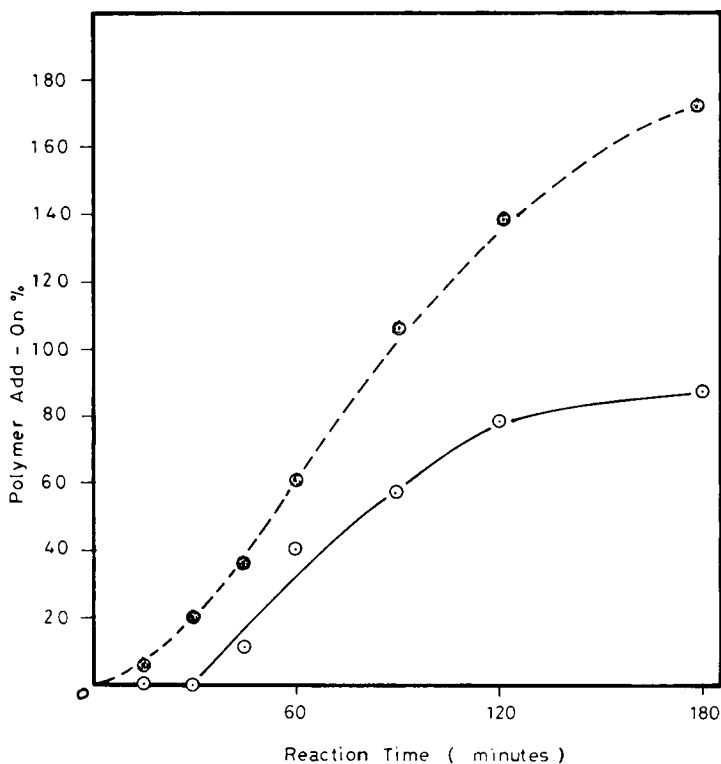
Fig. 4. Rate of polymerization of AMA with wool using benzoyl peroxide as initiator. [AMA], 147.4 mmol/L; material to liquor ratio, 1:100; benzoyl peroxide concn, 2 mmol/L; temp, 65°C. (—) In absence of Fe^{3+} ion; (------) in presence of Fe^{3+} ion.

Stability of the Allyl Double Bond

Samples of wool fabric containing different poly(AMA) add-ons were analyzed for the allyl double bond. The polymer add-ons which originally derived from the increase in weight of the fabric samples were recalculated on the basis of the allyl double bond analysis.

Table II shows variation of the remained double bond with the polymer add-on when the latter were induced by using different initiators. It is seen that the remaining double bond depends upon the magnitude of the polymer add-on; the higher this magnitude is, the lower the remaining double bond. This implies (a) that the allyl double bonds undergo homopolymerization reaction, i.e., crosslinking, and (b) that possible occurrence of crosslinking is favored at higher polymer add-on. Another additional point of interest is that the magnitude of crosslinking is also dependent upon the type of initiator. At roughly equal polymer add-on (e.g., 30% ± ca. 2%), the remaining double bond follows the order

$$\text{persulphate} > V^V > Fe^{2+}/H_2O_2 > Ce^{IV} > BP$$
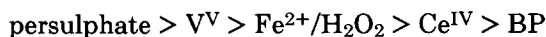
In short, the remaining double bond is governed by the magnitude of the polymer add-on as well as by the type of initiator.

TABLE II
Dependence of Remaining Double Bond in Wool Polymerized with Poly(AMA) on Percent Polymer Add-on and Type of Initiator

Pentavalent vanadium		$S_2O_8^-$		Benzoyl peroxide		AN		H_2O_2/Fe^{++}	
Polymer add-on (%)	Remaining double bond (%)	Polymer add-on (%)	Remaining double bond (%)	Polymer add-on (%)	Remaining double bond (%)	Polymer add-on (%)	Remaining double bond (%)	Polymer Add-on (%)	Remaining double bond (%)
8.7	94.2	10	85.00	5.3	89.4	6.3	66.5	17.5	32.5
10	84.4	26.4	47.7	27.7	6.2	17.6	40.5	31.00	9.35
30	35	32.00	35.8	106.5	2.3	23.7	17.0	39.00	11.3
36.7	13.6	35.00	30.00	163.6	0	32.00	8.1	51.00	6.8
49.2	5.44								

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