# Graft Copolymer from Modified Ethylene−Vinyl Acetate (EVA) Copolymers. 3. Poly(EVA-*g*-Methyl Methacrylate) from Mercapto-Modified EVA

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ABSTRACT: This paper describes a new route for synthesis of poly(ethylene-*co*-vinyl acetate-*g*-methyl methacrylate) (EVA-*g*-PMMA) based on free radical polymerization of methyl methacrylate initiated by azobis(isobutyronitrile) (AIBN), in the presence of mercapto-modified EVA as chain transfer agent. This functionalized EVA, namely, poly(ethylene-*co*-vinyl alcohol-*co*-vinyl mercaptoacetate) (EVASH) is prepared by simple esterification of hydrolyzed EVA with mercaptoacetic acid. Higher conversions of grafted poly(methyl methacrylate) (PMMA) were obtained by increasing the [SH]/[AIBN] ratio. In addition, a uniform molecular weight distribution of PMMA segments in the graft and a higher thermal stability of the graft copolymer can be achieved by controlling the [AIBN]/[SH] ratio. The PMMA segments in the graft copolymer do not affect the crystallinity degree of the EVASH backbone, as indicated by differential scanning calorimetry (DSC) analyses.

## Introduction

Graft copolymers based on ethylene−vinyl acetate copolymers have been prepared to improve mechanical properties of several brittle polymers such as poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), and polystyrene (PS). Most of these techniques involve the addition of free radical initiators in a mixture of ethylene−vinyl acetate (EVA) and the monomer to be grafted.[1,2] The presence of acetate groups along the EVA backbone increases the number of branching points. Indeed, the grafting efficiency on EVA is about 30 wt % greater than that on polyethylene, in reactions performed at the same conditions.[2] Using azobis(isobutyronitrile) (AIBN) as initiator, the polymerization of styrene or methyl methacrylate presents low conversion and low grafting efficiency. This graft copolymerization system does not permit an effective control of grafting points and consequently a good control of the average number of grafted chains.

The introduction of specific reactive sites along the EVA backbone constitutes a good option for developing EVA graft copolymers with more controllable molecular weight and molecular weight distribution of grafted chains. Esterification of hydrolyzed EVA with *p*-nitrobenzoyl chloride[3] or mercaptoacetic acid[4] are good examples of introducing reactive sites for further graft polymerization. In both cases, the added groups act as chain transfer agents, initiating the styrene graft polymerization by free radical mechanism.

When the aim of graft copolymerization is polymer synthesis, it is desirable to achieve good conversion into polymer material. In this sense, the system involving mercapto-modified EVA (EVASH) should be preferred. Indeed, high conversion and high grafted polystyrene conversion were achieved after 32 h of reaction.[4]

Considering the good results obtained on styrene graft polymerization, we decided to extend our studies using methyl methacrylate as a monomer. This work concerns the synthesis of poly(ethylene-*co*-vinyl acetate-*g*-methyl methacrylate) (EVA-*g*-PMMA) by using MMA/AIBN/EVASH. This material may have an important role in compatibilization of several commercial polymers that include EVA/PMMA, EVA/PVC, and EVA/styrene−acrylonitrile copolymer (SAN) blends.

## Experimental Section

**Materials.** Methyl methacrylate (MMA) was distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol/water (1:1). Mercaptoacetic acid (MAA) was distilled under reduced pressure and stored under nitrogen at −20 °C. Ethylene−vinyl acetate copolymer (EVA), supplied by Petroquímica Triunfo S. A., has a vinyl acetate content of 18 wt % and a melt flow index of 2.1 g/(10 min) at 200 °C.

**Procedures.** EVA copolymer was hydrolyzed in homogeneous medium (5.0 wt % solution in toluene), using 0.1 mol % of sodium methoxide (10.0 wt % solution in methanol).[5] The reaction was carried out under reflux for 60 min. The total hydrolysis was confirmed by infrared spectrometry.

The corresponding ethylene−vinyl alcohol (EVOH) was modified with mercaptoacetic acid, according to literature.[4,6] SH content on the corresponding poly(ethylene-*co*-vinyl alcohol-*co*-vinyl mercaptoacetate) (EVASH) was determined by titration of nonreacted MAA remaining in the methanolic layer with standardized 0.05 N NaOH methanolic solution.

The graft copolymerization was carried out in a two-necked flask equipped with a nitrogen inlet and stopcock for reagent addition. Thus, 20 g of EVASH was dissolved in 200 mL of toluene at 60 °C. Then, predetermined amounts of MMA and AIBN were added. After a preestablished reaction time, the material was poured into methanol, filtered, washed several times with methanol, and dried.

Nongrafted PMMA was removed by extraction with acetone in a Soxhlet apparatus for 6 h.

For determination of conversion and molecular weight of grafted PMMA, a known amount of graft copolymer (acetone-insoluble fraction) was dissolved into hot toluene and submitted to reaction with 1.0 wt % sodium methoxide solution under reflux for 60 min. With this treatment the grafted PMMA separates from the EVA backbone through transesterification reaction. After reextraction with acetone, the isolated PMMA was weighted and analyzed by size exclusion chromatography (SEC).

The average number of PMMA chains in the graft was calculated from the ratio between PMMA conversion as a graft and the average number molecular weight, $M_n$, as follows:

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$$P = \frac{[PMMA]_{graft}}{\overline{M}_n}$$

The chain transfer constant of SH groups in the EVASH backbone, Cs, was calculated according to the following relationship:[7]

$$(1 - \alpha)^{Cs} = [SH]/[SH]_0$$

where α is the fractional conversion of the monomer; Cs, the chain transfer constant; [SH], the SH concentration after a period of polymerization; and $[SH]_0$, the initial SH concentration.

The grafting efficiency was calculated by the relationship:

$$G_{eff} = 100(P/[SH]_0)$$

**Characterization.** The infrared spectroscopy analysis was made on a Perkin-Elmer FTIR spectrometer, Model 1600. The molecular weights of the polymeric material were determined with a 600E Waters high-speed liquid chromatograph, equipped with a 910 refractive index detector, a 940 diode-array ultraviolet detector, and four ultrastyragel columns ($10^5$, $10^4$, $10^3$, and 500 Å porosity) using tetrahydrofuran (THF) as a solvent. The values of $M_n$ and molecular weight distribution (MWD) were obtained by calibration with polystyrene standards. DSC analyses were performed with the help of a Perkin-Elmer DSC-7 calorimeter using the following conditions: the samples were heated at 10 °C/min to 200 °C, then cooled at 10 °C/min to 25 °C, and heated again at the same rate for a second time. The peak maximum from the DSC melting thermograms was considered as the melting point. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer TGA-7, under nitrogen, with a heat velocity of 20.0 °C/min. $^1$H-NMR spectra were run on a 300 MHz Varian instrument in toluene-$d_8$ at 80 °C.

## Results and Discussion

**Synthesis of Poly(EVA-*g*-methyl methacrylate).** The synthetic pathway providing graft copolymerization of methyl methacrylate from mercapto-modified EVA (EVASH) is illustrated in Figure 1. In all of the reactions, the polymer was separated into acetone-soluble and -insoluble fractions in a Soxhlet extractor. This method was effective for isolating the PMMA from a blend of EVASH and PMMA homopolymers and also effective for separating PMMA homopolymer from EVA-*g*-PMMA with a percentage of PMMA as high as 80 wt %. Thermogravimetric analysis of the acetone extract showed only PMMA decomposition peaks, indicating no soluble graft copolymer in acetone. This analysis will be discussed later.

The quantitative analysis of copolymer composition was made gravimetrically and confirmed by $^1$H NMR analysis. The acetone-insoluble fraction is soluble in toluene at 70 °C. Figure 2 shows the $^1$H NMR spectra of two representative acetone-insoluble samples with different graft content and the corresponding homopolymers in toluene-$d_8$ at 70 °C. The experimental conditions and graft copolymer features will be discussed later. The $^1$H NMR spectrum of PMMA presents chemical shifts at 3.3, 1.9, and 1.1−1.2 ppm, corresponding to methoxy groups ($CH_3O$), methylene groups ($CH_2C$), and methyl groups ($CH_3C$), respectively. Concerning the EVASH spectrum, the chemical shifts at 2.0 and 1.3 ppm correspond to methine and methylene groups in EVASH. It was not possible to detect the signals related to SH or OH because of the low concentration of these groups in the copolymer. As observed in the top two spectra of Figure 2, the peaks related to EVASH appear at the same chemical shifts as those of

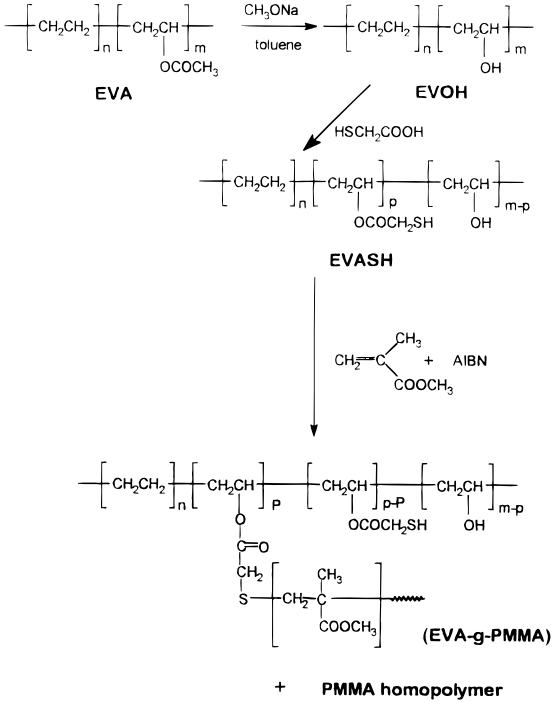


**Figure 1.** Synthetic pathway for preparation of poly(ethylene-*co*-vinyl acetate-*g*-methyl methacrylate) (EVA-*g*-PMMA).

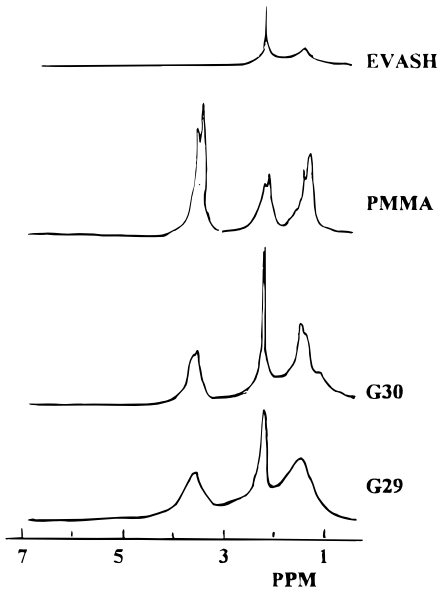


**Figure 2.** $^1$H-NMR spectra of EVASH, PMMA, and two representative graft copolymers (G29 and G30). The characteristics of graft copolymers are presented in Table 2.

PMMA. Thus, the quantitative analysis of the copolymers was calculated from a theoretical calibration curve where the ratio between methoxy protons ($CH_3O$) related to PMMA and the other methyl and methylene protons from PMMA and EVASH are plotted against the corresponding composition in mole percent, as illustrated in Figure 3. The relationship between protons, Rp, indicated in the Figure 3 plot, is calculated as follows:

$$Rp = [CH_3O]_{PMMA}(\text{mol \% PMMA})/\{[CH_3 + CH_2]_{PMMA}(\text{mol \% PMMA}) + 2[CH_2]_{EVASH}(\text{mol \% EVASH})\}$$

The ratio of the two integrated intensities between $\delta$ = 3.3 ppm (related to PMMA) and $\delta$ = 1.1−2.0 ppm

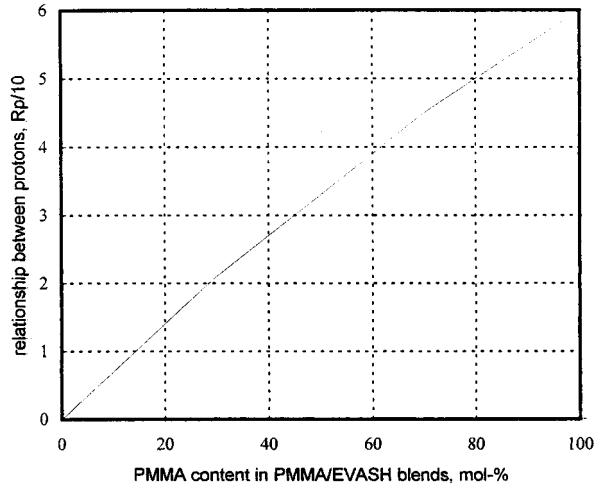


**Figure 3.** Calibration curve for determination of copolymer composition based on $^1$H-NMR analyses.

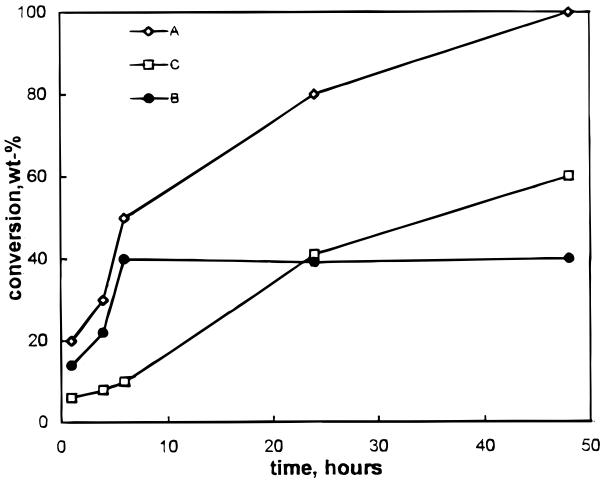


**Figure 4.** Effect of polymerization time on PMMA conversion: (A) total conversion; (B) PMMA homopolymer conversion; (C) conversion of PMMA as a grafted chain (reaction conditions described in Table 1).

(related to PMMA and EVASH) was related to the copolymer composition in Figure 3 to determine the mole percentage of PMMA in the copolymer.

Figure 4 illustrates the effect of polymerization time on conversion. A preferential PMMA homopolymer formation is observed during the first 6 h of reaction. The proportion of grafted PMMA surpasses the PMMA homopolymer when the overall polymer conversion reaches high values.

Table 1 presents the characteristics of EVA-*g*-PMMA as a function of polymerization time. Decreasing molecular weight of nongrafted PMMA with the time is observed. According to literature,[8] this behavior suggests a chain transfer constant to EVASH, Cs, of nearly 0.1. Indeed, the calculated Cs values are in agreement with the theory stated by Sato and Okaya.[8] The chain transfer constant in MMA polymerization in the presence of ethyl mercaptoacetate is reported to be 0.63.[9] The lower values found in our experiments can be attributed to the poor SH accessibility due to the natural coiling of the EVASH chains in solution. The poor SH accessibility also results on an increase of graft PMMA molecular weight at the beginning of the reaction. The free radical growing species derived from homopolymerization can hardly reach the SH groups. When some free radical branching points on EVASH are formed, the

**Table 1. Effect of Reaction Time on Synthesis of Poly(EVA-*g*-methyl Methacrylate)[a]**

| time (h) | grafted PMMA $M_n \times 10^{-3}$ | grafted PMMA $P^b$ (mmol) | $M_n$ of PMMA homopolym $\times 10^{-3}$ | [S][c] (mmol) | Cs[d] | graf efficiency[e] (%) |
|---|---|---|---|---|---|---|
| 1 | 16.6 | 0.18 | 27.1 | 5.4 | 0.14 | 3 |
| 4 | 30.7 | 0.12 | 23.3 | 5.46 | 0.06 | 2 |
| 6 | 27.1 | 0.19 | 21.3 | 5.39 | 0.05 | 3 |
| 24 | 12.4 | 1.68 | 13.5 | 3.9 | 0.22 | 30 |
| 48 | 8.0 | 3.81 | 12.9 | 1.77 | | 68 |

[a] Reaction conditions: EVASH, 20 g (5.58 mmol SH); MMA, 56.6 g (0.56 mol); AIBN, 5.487 mmol; toluene, 300 mL; temperature, 60 °C. [b] Average amount of grafted chain calculated as described in Experimental Section. [c] [S] = SH concentration at the time; [S] = $[S]_0 - P$. [d] Cs = chain transfer constant calculated as described in Experimental Section. [e] Graft efficiency, $G_{eff}$, calculated as described in Experimental Section.

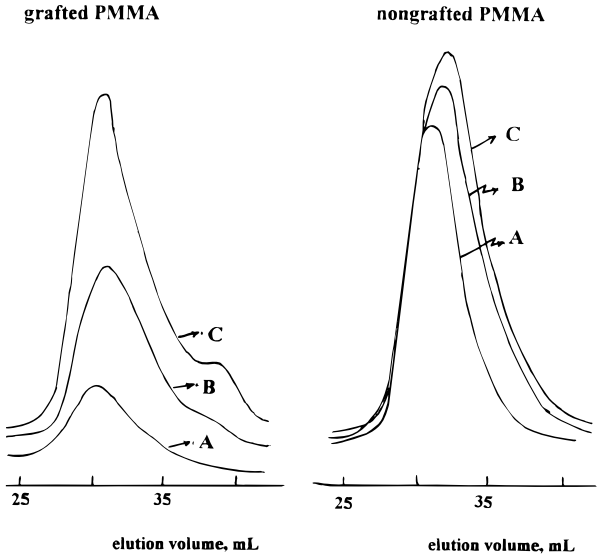


**Figure 5.** SEC curves of grafted and nongrafted PMMA at (A) 6, (B) 24, and (C) 48 h of reaction (reaction conditions described in Table 1).

graft propagation takes place, increasing the molecular weight. As the incorporation of MMA in EVASH increases, the solubility of the copolymer also increases. Thus, the SH groups along the backbone become more available for transfer reaction, resulting in an increase of graft efficiency. This behavior also influences the molecular weight distribution profile of the grafted PMMA, as shown in Figure 5. Indeed, a small amount of low molecular weight chains forms at the end of the polymerization process as a consequence of increasing the SH accessibility.

Table 2 presents the graft copolymerization results obtained with different polymerization parameters. For experiments with fixed AIBN and MMA concentrations (runs G5 and G9), increasing SH concentration increases the overall MMA conversion into polymeric material and also the graft efficiency while decreasing the molecular weight of grafted PMMA. Both reaction conditions lead to the same amount of homopolymer, probably as a consequence of the same MMA/AIBN ratio being employed. In both experiments, the concentration of free radical growing species derived from homopolymerization should be comparable. Therefore, the decrease in graft efficiency in run G5 may be due to the difficulty of these growing species in reaching the SH groups, present in a very low concentration.

Runs G29 and G30 present different behavior. Although the SH concentration on EVASH is higher than

**Table 2. Summary of EVA-*g*-PMMA Copolymers and Reaction Conditions[a]**

| run | EVASH (mmol) | AIBN (mmol) | [AIBN]/[SH] | conversion: total (wt %) | conversion: grafted PMMA[b] (wt %) | conversion: grafted PMMA[b] (mol %) | conversion: nongrafted PMMA[c] (wt %) | $M_n \times 10^{-3}$: grafted PMMA[d] | $M_n \times 10^{-3}$: nongrafted PMMA | $P^e$ (mmol) | $G_{eff}^f$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| G5 | 1.84 | 5.49 | 2.98 | 50 | 10 | 3 | 40 | 33.2 | 8.8 | 0.17 | 9 |
| G9 | 5.58 | 5.49 | 0.98 | 100 | 60 | 30 | 40 | 8.0 | 12.9 | 3.80 | 68 |
| G29 | 9.2 | 2.32 | 0.25 | 100 | 70 | 40 | 30 | 29.1 | 37.3 | 1.36 | 15 |
| G30[g] | 9.2 | 2.32 | 0.25 | 100 | 80 | 55 | 20 | 19.5 | 23.5 | 0.93 | 10 |

[a] Reaction conditions: MMA, 56.6 g (0.566 mol); EVASH, 20 g; toluene, 300 mL; time, 48 h; temperature, 60 °C. [b] Acetone-insoluble fraction. [c] Acetone-soluble fraction. [d] Determined from SEC analysis of PMMA after treatment of graft copolymer with sodium methoxide (see Experimental Section). [e] $P$ = average number of PMMA chain as graft, determined as described in Experimental Section. [f] $G_{eff}$ = grafting efficiency, determined as described in Experimental Section. [g] MMA, 22.7 g (0.227 mol).

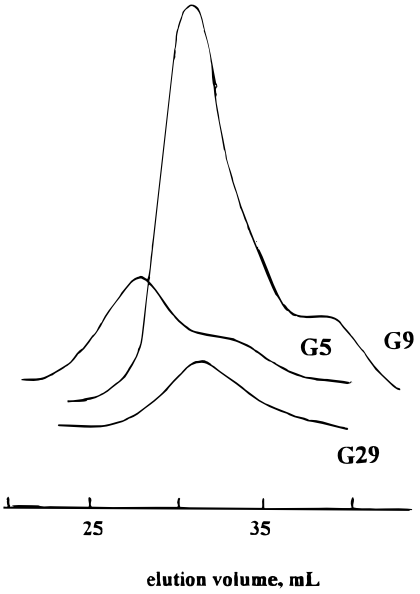


**Figure 6.** SEC curves of grafted PMMA in graft copolymers prepared at different conditions (reaction conditions described in Table 2).

that employed in run G9, the graft efficiency decreases. It is important to point out the lower AIBN concentration employed in these experiments, which contributes to decreasing the free radical concentration able to abstract hydrogen atoms of SH groups along the EVASH backbone. Consequently, the concentration of free radical branching points on EVASH will be lower. These features result also in higher molecular weights of both grafted and nongrafted PMMA, in spite of a higher transfer agent concentration.

Run G30 presents a lower molecular weight value when compared to run G29, due to the lower monomer concentration employed. In this case, the PMMA/EVASH weight ratio in the graft copolymer is lower. Considering that PMMA chains have more affinity with the solvent than EVASH, a decrease in the PMMA amount in the copolymer increases the coiling of the chain, which diminishes the SH accessibility. These differences in chain conformation of the copolymer as a result of the PMMA proportion may be responsible for the differences in the average number of grafted chains, $P$, and, consequently, the graft efficiency.

Figure 6 presents the SEC curves of grafted PMMA obtained after treatment of graft copolymer with sodium methoxide followed by isolation of PMMA chains. A more uniform molecular weight distribution of grafted PMMA is observed in reactions performed at lower AIBN concentration (run G29). At higher AIBN concentration (runs G5 and G9), the SEC curves present an almost bimodal shape. This behavior can be attributed to a higher [AIBN]/[SH] molar ratio used in these experiments. A decreasing [AIBN]/[SH] molar ratio increases the chain transfer velocity to SH groups, giving rise to more uniform grafted segments.

## Thermal Analyses

**Thermal Degradation.** It is reported that the thermal degradation of radically synthesized PMMA occurs in two main stages.[10] The first one occurs around 270 °C and is characterized by a radical chain unzipping reaction initiated at unsaturated chain ends. The second step at around 300 °C involves random degradation along the polymer chain. The extent of each stage depends on the [MMA]/[AIBN] molar ratio, as pointed out by Rychly and Pavlinec.[10] Considering the different features of SEC traces observed for grafted PMMA, it was decided that the thermal degradation of these graft copolymers as a function of reaction conditions would be studied.

Figure 7 illustrates the non-isothermal differential thermogravimetric (DTG) curves of EVA-*g*-PMMA prepared under different conditions, together with the corresponding homopolymers. The PMMA sample shown in Figure 7A corresponds to the acetone-soluble fraction of run G29. Parts C and D of Figure 7 represent the DTG curves of EVA-*g*-PMMA (runs G5 and G9, respectively), prepared with the same AIBN concentration but different SH content in EVASH. The degradation peaks around 400 and 500 °C are attributed to PMMA and EVASH segments, respectively, by comparison with the DTG curves of the corresponding homopolymers (Figure 7A,B). The degradation profiles of PMMA chains in the graft copolymer related to G9 are similar to those observed for PMMA homopolymer. Indeed, two main degradation peaks are observed around 300 °C and 400 °C, corresponding to typical PMMA degradation, as reported in the literature.[10] As determined by other analytical methods ($^1$H NMR spectrometry and gravimetry), run G5, prepared from EVASH with low SH content, presents a low incorporation of MMA as a graft. This result is confirmed by TGA (Figure 7C).

Concerning graft copolymers prepared with lower AIBN concentration (G29 and G30), an interesting behavior is observed. The degradation peak related to PMMA segments shifts to higher temperature (Figure 7E,F). In addition, there is no degradation around 300 °C, as observed in other samples.

The first step degradation of PMMA segments at 300 °C observed in sample G9 may be related to low molecular weight grafted chains. As illustrated above (Figure 6), this sample presents a significant low molecular weight fraction.

Figure 8 compares the DTG curves of graft copolymer (acetone-insoluble fraction) and the corresponding PMMA

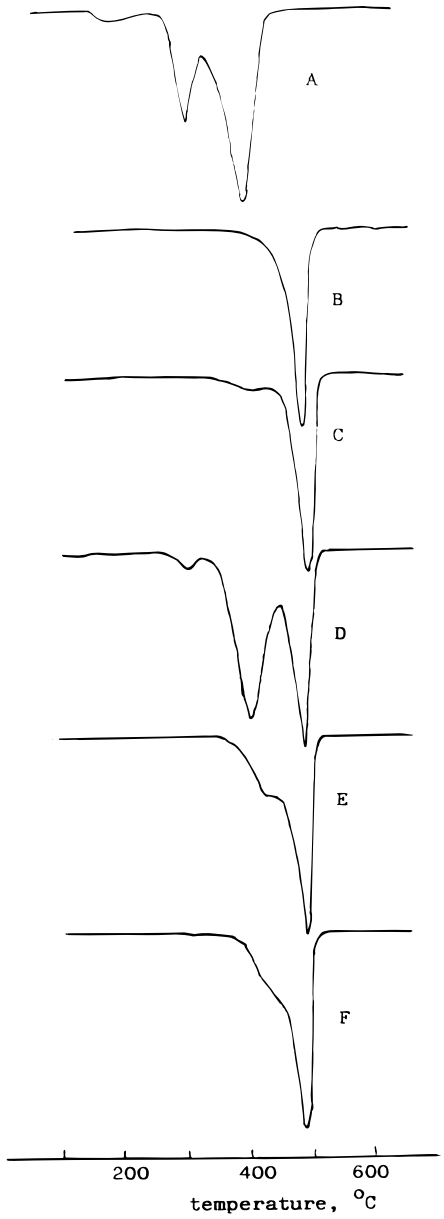


**Figure 7.** Non-isothermal differential thermogravimetric curves of (A) PMMA, (B) EVASH, (C) G5, (D) G9, (E) G29, and (F) G30 (reaction conditions described in Table 2).

homopolymer (acetone-soluble fractions) for reactions performed at different AIBN concentrations. Reaction performed at a lower AIBN concentration (run G29) gives rise to a graft copolymer whose PMMA segment thermal stability is higher than the corresponding homopolymer. Even for reactions performed at higher AIBN concentration (run G9), the extent of the first step degradation of PMMA segments (300 °C) in the graft copolymer is lower than that observed for the acetone-soluble fraction.

In graft copolymerization in the presence of EVASH, it is believed that the initiator first attacks the monomer, initiating a MMA polymerization. These growing free radical chains abstract a hydrogen atom from SH groups along the EVASH backbone, generating new free radicals on the EVASH which initiate the graft copolymerization. According to this mechanism, most of the initiator moiety ends are located in the homopolymer chains, which may be responsible for the lower thermal stability observed in these acetone-soluble fractions, as suggested in the literature.[10]

If the graft copolymerization from EVASH backbone takes place mainly through transfer reactions to SH groups, there are few initiator moiety ends on the PMMA grafted chains. Then, the lower thermal stability of grafted segments in run G9 may be attributed to the low molecular weight fraction of the grafted chain, formed during the polymerization process. In addition, it is important to emphasize that runs G29 and G30 are characterized by a lower grafting efficiency, as compared to run G9. As the initial SH concentration in runs G29 and G30 is higher, there are a lot of free SH groups in the EVASH backbone. These free SH groups may also be responsible for the PMMA stabilization. All these hypotheses need to be confirmed by preparing these graft copolymers through other polymerization techniques and studying the thermal degradation of the corresponding copolymers. These techniques may involve the synthesis of end-functionalized PMMA by anionic mechanism and the subsequent coupling reaction with hydrolyzed EVA. These studies are in preparation in our laboratory and will be published sooner.

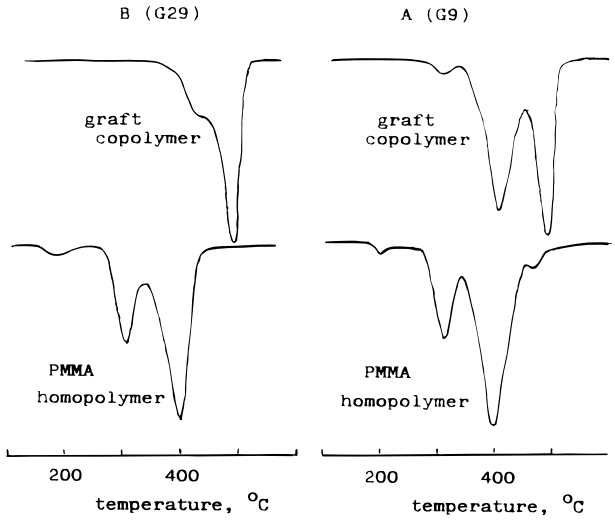


**Figure 8.** Non-isothermal differential thermogravimetric curves of graft copolymers (acetone-insoluble fraction) and the corresponding PMMA homopolymer (acetone-soluble fraction). (A) G9 and (B) G29 (reaction conditions described in Table 2).

**Melting and Crystallization Behaviors.** The graft copolymer studied in this report consists of a semicrystalline EVASH backbone carrying grafted amorphous polymer chains (PMMA). Thus, the effect of grafting on melting and crystallization behaviors of the EVASH backbone was also studied by DSC. Figure 9 presents the melting endotherm of graft copolymers containing 10 and 60 wt % PMMA and the corresponding physical blends. The corresponding cooling thermograms are shown in Figure 10. Both melting ($T_m$) (Figure 9B,C) and crystallization ($T_c$) (Figure 10B,C) temperatures of the EVASH phase are not affected by blending or grafting when the proportion of PMMA is low. With an increase in the PMMA proportion, a slight decreasing of the melting temperature of the EVASH phase in the graft copolymer vs the physical blend is observed in Figure 9E. This phenomenon is more pronounced during cooling, as indicated in Figure 10E. A decrease of $T_c$ with grafting indicates that the presence of PMMA segments affects the crystallization of the EVASH backbone. Similar results were observed by Liu and coworkers in studies of crystallization of poly(vinyl alcohol)-*g*-poly(methyl methacrylate) copolymers.[11]

The heats of fusion ($\Delta H_f$) and crystallization ($\Delta H_c$) are not substantially influenced by grafting reactions, when compared with theoretical values. Table 3 presents the

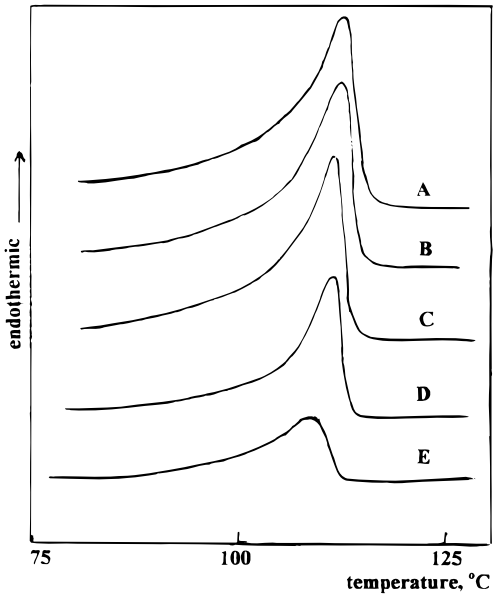


**Figure 9.** Melting endotherm of (A) EVASH, (B) EVASH/PMMA (90:10 wt %) blend, (C) EVASH-*g*-PMMA (90:10 wt %), (D) EVASH/PMMA (40:60 wt %) blend, and (E) EVASH-*g*-PMMA (40:60 wt %) (summary of DSC results presented in Table 3).

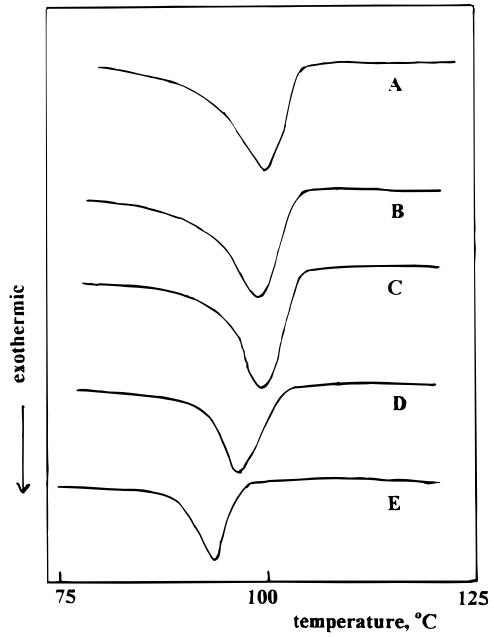


**Figure 10.** Cooling thermograms of (A) EVASH, (B) EVASH/PMMA (90:10 wt %) blend, (C) EVASH-*g*-PMMA (90:10 wt %), (D) EVASH/PMMA (40:60 wt %) blend, and (E) EVASH-*g*-PMMA (40:60 wt %), (summary of DSC results presented in Table 3).

results concerning the temperature and heats of fusion and crystallization as well as the relative percent crystallinities of EVASH in blends or as the graft copolymer backbone. The term "percent crystallinity" is used to denote the amount of crystallinity of a particular system (blend or graft copolymer) compared to pure EVASH. This term is calculated from the ratio between the $\Delta H_f$ of the EVASH/PMMA blend or graft and the $\Delta H_f$ of pure EVASH, taking into account the weight percentage of EVASH in the system. For example, the EVASH/PMMA (90:10 wt %) blend would have a theoretical $\Delta H_f$ value of 78.07 J/g, considering the amount of this polymer in the blend. This value is assumed to be 100% crystallinity.

**Table 3. Summary of DSC Results of EVASH/PMMA Blends and EVA-*g*-PMMA Graft Copolymers**

| | | EVASH/PMMA blends | | EVASH-*g*-PMMA | |
|---|---|---|---|---|---|
| | EVASH | 90:10 wt % | 40:60 wt % | 90:10 wt % | 40:60 wt % |
| *T*m (°C) | 111.7 | 111.8 | 110.7 | 110.8 | 108.5 |
| $T_c$ (°C) | 99.6 | 98.9 | 96.2 | 99.2 | 93.1 |
| $\Delta H_f$ (J/g) | | | | | |
| expt | 86.75 | 63.45 | 42.93 | 74.46 | 32.5 |
| theor[a] | | 78.07 | 34.70 | 78.07 | 34.70 |
| $\Delta H_c$ (J/g) | | | | | |
| expt | 82.43 | 65.95 | 38.15 | 74.26 | 29.75 |
| theor[a] | | 74.19 | 32.97 | 74.19 | 32.97 |
| relative Xc[b] (%) | 100 | 81 | 124 | 95 | 94 |

[a] $\Delta H$(theor) calculated from $\Delta H$ of pure EVASH, taking into account the weight percentage of EVASH in the blend or in the graft copolymer. [b] Xc = percent crystallinity related to EVASH content in the blend or in graft copolymer. Xc = 100($\Delta H_f$(expt)/$\Delta H_f$(theor).

The crystallinity degree of PMMA/EVASH blends has different behavior, depending on the polymer composition. For high PMMA content (60 wt %), the crystallinity degree is higher than the theoretical one. On the other hand, for lower PMMA content (10 wt %) the crystallinity degree decreases, which can be explained by a better dispersion of PMMA into an EVASH matrix.

The grafting process promotes a slight decrease in the crystallinity degree of the EVASH backbone, compared to theoretical values. The relative percent crystallinity is not affected by the extent of grafting.

## Conclusion

The use of mercapto-modified EVA as a chain transfer agent in methyl methacrylate free radical polymerization is a good way to synthesize a graft copolymer with high conversion to grafted PMMA. A more uniform molecular weight distribution can be achieved by controlling the [AIBN]/[SH] molar ratio. The experiments performed with lower [AIBN]/[SH] molar ratio leads to graft copolymers with higher thermal stability of the grafted PMMA, as observed in thermogravimetric analyses. As suggested in literature,[10] a higher PMMA thermal stability is achieved in MMA polymerizations carried out with a higher [monomer]/[AIBN] ratio. In our system, the thermal stability may be influenced by the presence of SH groups in the EVASH backbone. Indeed, the [MMA]/[AIBN] molar ratio employed in run G30 is similar to that in run G9. Nevertheless, the [SH]/[AIBN] molar ratio used in G30 is higher, contributing to its stability. Increasing AIBN concentration increases also the graft efficiency, but the molecular weight distribution of grafted segments is not uniform. Nevertheless, even when AIBN concentration is high, the graft efficiency is very low when the EVASH sample contains very low SH concentration, as observed in run G5.

The nonuniformity of molecular weight in these segments and the lower thermal stability of the graft copolymer may be hazardous if these copolymers will be employed for blend compatibilization. As most technological polymer blends are produced in melt, a decrease in thermal stability of the compatibilizing agent may affect the mechanical properties of the material. Thus, it is important to achieve the best [monomer]/[AIBN]/[SH] relationship and the best reaction conditions to improve the graft efficiency and conversion into grafted chains without affecting the

chemical structure and thermal properties of the copolymer. The crystallinity degree of EVASH backbones is not substantially influenced by PMMA segments in the copolymer, compared with theoretical values. Considering systems with a higher PMMA amount, both blend and graft copolymers present a decrease in crystallization temperature. This effect is more pronounced with the graft copolymer, probably due to poorer EVASH chain organization.

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