Graft Copolymers from Modified Ethylene–Vinyl Acetate (EVA) Copolymer. I. Synthesis of Poly(ethylene-*co*-vinyl acetate-*g*-styrene) Using EVA Modified by Mercaptoacetic Acid as Chain Transfer Agent

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SYNOPSIS

The modification of the poly(ethylene-*co*-vinyl acetate) (EVA) by direct esterification of its ethylene–vinyl alcohol copolymer with mercaptoacetic acid was carried out. The amount of the mercaptan group was controlled to avoid gel formation during the graft polymerization with styrene by chain transfer. The chain transfer constant (*Cs*) of the SH groups and graft efficiency were measured. These graft copolymers were evaluated as a blend compatibilizer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization of styrene onto polyethylene and poly(ethylene-*co*-vinyl acetate) (EVA) is reported in the literature. Locke and Paul used the radiation technique to graft styrene to low-density polyethylene (LDPE).[1] Barensten and Heikens used Friedel–Crafts alkylation of polystyrene with LDPE.[2,3] In both cases, attempts were made to characterize these grafts but no definite measures of the length of the grafts or their frequency on the backbone were found.[4] Pilz used X-ray radiation for grafting styrene on EVA.[5] Nakamura et al. used modified EVA, obtained by the esterification of ethylene–vinyl alcohol copolymer with *p*-nitrobenzoyl chloride for the graft copolymerization of styrene onto ethylene–vinyl–*p*-nitrobenzoate copolymer by chain transfer reaction.[6]

It is well known that mercaptans have a high chain transfer constant with a variety of monomers. This property has been used by Graham and coworkers in the synthesis of graft copolymers of styrene onto poly(methyl methacrylate) having a pendant mercaptan group.[7]

In this paper, we present an improved method for the preparation of poly(ethylene-*co*-vinyl acetate-*g*-styrene) (EVA-*g*-PSty) using EVA modified by mercaptoacetic acid as the chain transfer agent.

EXPERIMENTAL

Materials

Ethylene–vinyl alcohol copolymer (EVAL) was obtained by the hydrolysis of ethylene–vinyl acetate copolymer with a vinyl acetate content of 20.2 mol % and MW of 80,000 (a commercial product of Politeno S.A.) in toluene with sodium methoxide. Styrene (free of an inhibitor) was distilled under reduced pressure. Azobisisobutironitrile (AIBN) was recrystallized from methanol/water (1:1). Mercaptoacetic acid (MAA) (Merck) was distilled under reduced pressure and stored under nitrogen at −20°C. The infrared spectroscopy analysis was made on a Perkin-Elmer Model 1720X. The molecular weights of the polymeric materials were determined with a Toyo-Soda high-speed liquid chromatograph HLC-803A equipped with an RI detector and two

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ultrastyragel columns (linear and 500A) using toluene as a solvent. The values of molecular weight and molecular weight distribution were obtained from polystyrene (PSty) calibration. ^{13}C-NMR spectra were performed on a Varian VXR 300 spectrometer in solution of $CDCl_3$.

Procedures

Ethylene–Vinyl Alcohol Copolymer Modified with Mercaptoacetic Acid (EVAL–SH)

In a two-necked flask equipped with a Dean-Stark apparatus, 20.0 g (0.1277 mol OH) of EVAL were dissolved in 300 mL toluene. MAA, 20.0 g (0.217 mol), was added to the flask, and the system was refluxed at a predetermined period. The EVAL–SH was then precipitated into degassed methanol, filtered under nitrogen, and washed several times with methanol. The material was dried by azeotropic distillation with toluene and stored in toluene solution at −20°C.

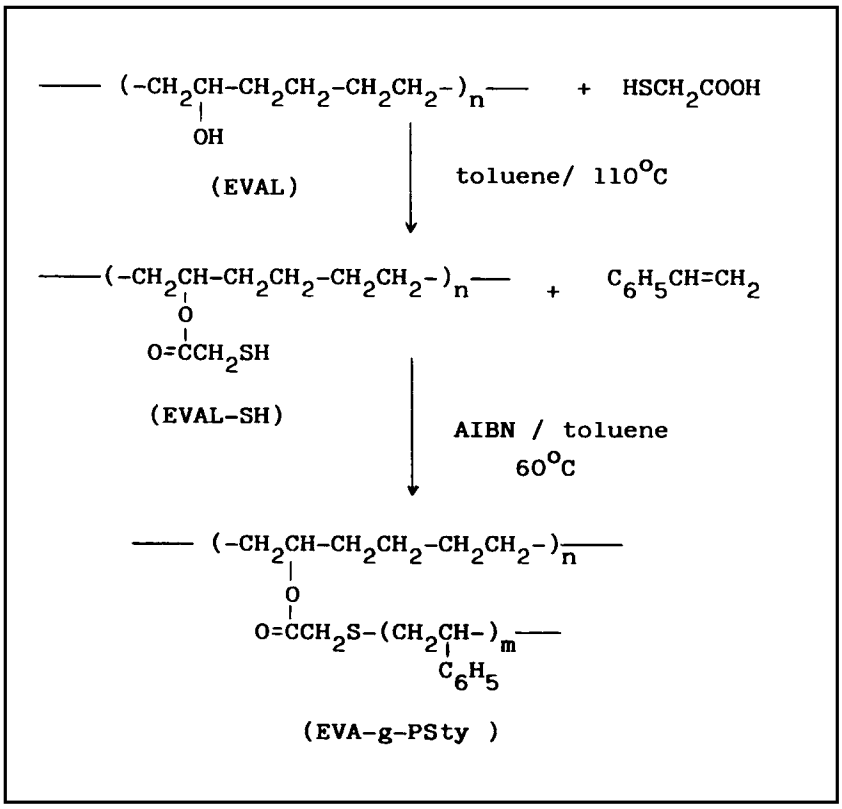
The SH content was determined by reacting a weighed sample of the polymer dissolved in 150 mL benzene with 15 mL of a 0.0988*N* solution of *n*-butyl mercaptan in benzene and 60 mL of a 0.05*N* solution of iodine in ethanol during 48 h in the dark. Titration was then carried out with standardized 0.056*N* sodium thiosulfate solution.

Graft Copolymerization

The synthesis of EVA-*g*-PSty was carried out in a two-necked flask equipped with a nitrogen inlet and a rubber septum for the aliquot withdrawn. Thus, predetermined amounts of EVAL–SH, styrene, and AIBN were dissolved in 40 mL toluene. The reaction was performed at 60°C and aliquots of the reaction were withdrawn at predetermined intervals. These aliquots were poured into degassed methanol, filtered, washed several times with methanol, and dried. Nongrafted PSty was removed by extraction with acetone, since cyclohexane gave poor separation of the graft copolymer from the PSty. The graft copolymer obtained was then dissolved in toluene and hydrolyzed with methanolic sodium hydroxide solution (10%) at 110°C for 1 h.

RESULTS AND DISCUSSION

Scheme I shows the preparation of EVA-*g*-PSty from EVAL.



Scheme 1 Steps employed during the preparation of EVA-*g*-PSty from EVAL.

Table I Preparation of EVAL–SH[a]

Exp. No.	Time (h)	Mercaptan Content[b] $\times 10^3$ (Mol/g)	Esterification Degree (%)	Copolymer Composition (%)		
				ET[c]	VAL[c]	VMA[c]
RS-4	5	2.36	37	79.8	12.7	7.5
RS-5	24	3.89	61	79.8	7.9	12.3

[a] Reaction conditions: EVAL: 20 g (0.1277 mol OH); MAA: 20 g (0.217 mol); temp: 110°C; toluene: 300 mL.
[b] Mercaptan content determined by iodometric titration.
[c] ET: ethylene; VAL: vinyl alcohol; VMA: vinyl mercaptoacetate.

Preparation of EVAL–SH

The conditions used for esterification of EVAL with MAA and the results obtained are summarized in Table I. The infrared spectra of these modified copolymers are shown in Figure 1, where the esterification reactions are confirmed. The absorption at 3500–3800 cm^{-1} related to the OH group diminishes, while the 1735 cm^{-1} absorption related to the carbonyl group appears. The sample RS^{-5}, which has a mercaptan content of 61% compared with the OH number of the EVAL backbone, presents a more accentuated carbonyl absorption.

Preparation of the Graft Copolymer EVA-*g*-PSty

The first attempts to polymerize styrene using EVAL–SH as the chain transfer agent were made

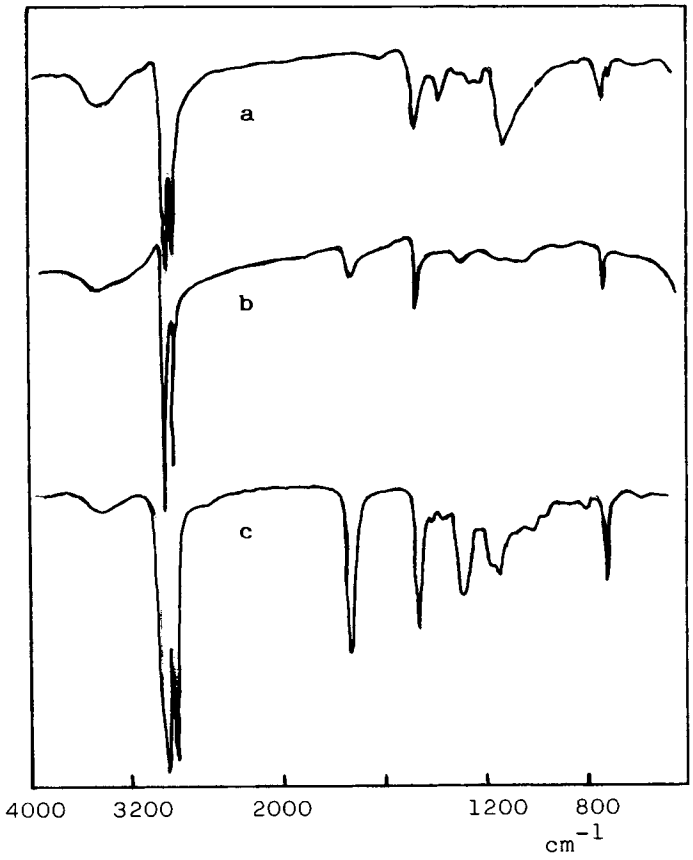


Figure 1 Infrared spectra of (a) EVAL, (b) RS-4 ([SH] = 7.5 mol %), and (c) RS-5 ([SH] = 12.3 mol %).

Table II Graft Copolymerization of Styrene onto EVAL–SH[a] [SH]/Polymer Chain = 12.2 Mol %

Exp. No.	Sty (Mol)	EVAL–SH (g)	[SH] $\times 10^3$ (Mol)	Time (h)	Toluene (mL)	Product Remarks
RG-1[b]	0.043	0.66	2.56	42	10	Gel
RG-7	0.043	0.66	2.56	1	20	Gel
RG-8	0.258	0.66	2.56	1	50	Gel

[a] AIBN: 0.42×10^{-3} mol; temp: 60°C.
[b] Reaction carried out in a sealed glass ampule previously degassed three times.

with the sample RS-5 ([SH]: 12.3 mol %). The reaction conditions are shown in Table II. In all experiments, cross-linked products were obtained even when the amount of monomer or solvent was increased several times. These results can be attributed to the high concentration of the SH group per polymer chain employed.

To avoid cross-linking, we decided to employ a sample of EVAL–SH with a lower content of the mercaptan group. The conditions for graft copolymerization in the presence of RS-4 ([SH]: 7.5 mol %) are described in Table III. At these conditions, no cross-linked product was observed. The polymeric material was totally soluble in hot toluene. After extraction with acetone for 5 h, an increase of weight in insoluble material (nonextracted) was observed compared with the trunk polymer EVAL–SH. Since styrene homopolymer is completely extracted with acetone, the increase of weight corresponds to PSty as graft. The percentage of PSty as graft increased with the time and so did the molecular weight. It was not possible to determine the molecular weight of the graft copolymer at 3 h of reaction time due to the insolubility of this material in toluene at room temperature. This fraction has a low content of PSty that makes it insoluble.

In Figure 2, the SEC curves of graft copolymer and styrene homopolymer are compared with the SEC curve of EVA used in the EVAL–SH preparation. It was not possible to analyze the EVAL–SH by SEC because of its insolubility in toluene at room temperature. EVA has a lower refractive index than does toluene (the solvent used in SEC analysis), so its chromatogram has an inverted shape. The graft copolymer, on the other hand, has a higher refractive index than does toluene because of the PSty branches along the backbone. The positive curve of the chromatogram of the insoluble material in acetone is strong evidence for grafting, although the molecular weight and MWD values cannot be determined accurately by SEC because of the negative contribution of the refractive index related to the EVA backbone.

In addition to the gravimetric and SEC analyses, more evidence that the nonextracted material consists of the graft copolymer is obtained by infrared

Table III Preparation of EVA-*g*-PSty Using EVAL–SH (SH = 7.4 mol %)[a]

Time (h)	Total Conversion of PSty (%)	Grafted PSty (%)	Nongrafted PSty (%)	$M_n \times 10^{-3}$ Graft PSty[b]	$M_n \times 10^{-3}$ Nongraft PSty	MWD Graft PSty[b]	MWD Nongraft PSty
3	7.3	2.8	4.5	6.2	4.9	2.50	1.75
6	12.5	6.3	6.2	10.8	7.2	2.33	2.00
9	16.7	7.7	9.0	12.9	9.4	2.69	2.69
24	55.5	33.3	22.2	29.7	10.7	1.62	2.15
32	100.0	80.0	20.0	34.0	10.6	1.46	1.80

[a] Reaction conditions: EVAL–SH: 0.6 g (1.413×10^{-3} mol SH); AIBN: 4.26×10^{-4} mol; styrene: 0.26 mol; toluene: 55 mL; temp: 60°C.
[b] Determined from SEC analysis of polystyrene after hydrolysis of the graft copolymer.

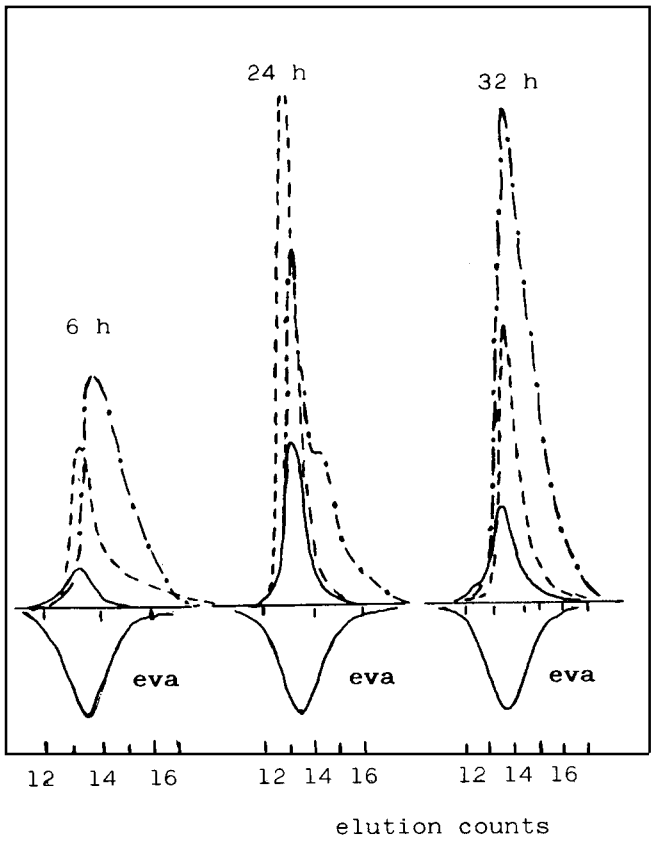


Figure 2 SEC chromatograms of (——, top) graft copolymer, (---) PSty as graft, (– · – · –) nongrafted PSty, and (——, bottom) EVA.

and ^{13}C-NMR analyses. The infrared spectra presented in Figure 3 show an accentuated absorption at 1730 cm^{-1} related to carbonyl groups of ester along the backbone and an absorption at 1601 cm^{-1} characteristic of the PSty chain, confirming the graft copolymerization. At the same time, the PSty fraction in the graft copolymer increases with the time reaction, while the carbonyl absorption decreases.

The ^{13}C-NMR spectra of the graft copolymers obtained after 9 and 24 h reaction are shown in Figure 4. Based on previous calculations taking into account the vicinity of the envolved carbon atoms, we can attribute the chemical shifts at 25.7, 33.89, and 37.61 ppm to the methylene groups as —$COCH_2SH$, $RSCH_2CO$—, and —C_6H_5CH—CH_2S—, respectively, as indicated in Figure 4.

Table IV Graft Efficiency and Percent Grafting in Synthesis of EVA-*g*-PSty Using EVAL–SH ([SH] = 7.4 mol %)[a]

Time (h)	Fractional Conversion (α)	$[SH]/[SH]_0$	C_s[b]	Percent Grafting	Graft Efficiency (%)
3	0.07	0.91	1.24	0.64	8.6
6	0.12	0.89	0.87	0.82	11.12
9	0.17	0.88	0.70	0.84	11.40
24	0.55	0.47	0.93	1.63	22.0
32	1.00	0.51	—	3.64	49.2

[a] Reaction conditions described in Table III.
[b] Calculated from the relationship $(1 - \alpha)^{C_s} = [SH]/[SH]_0$.

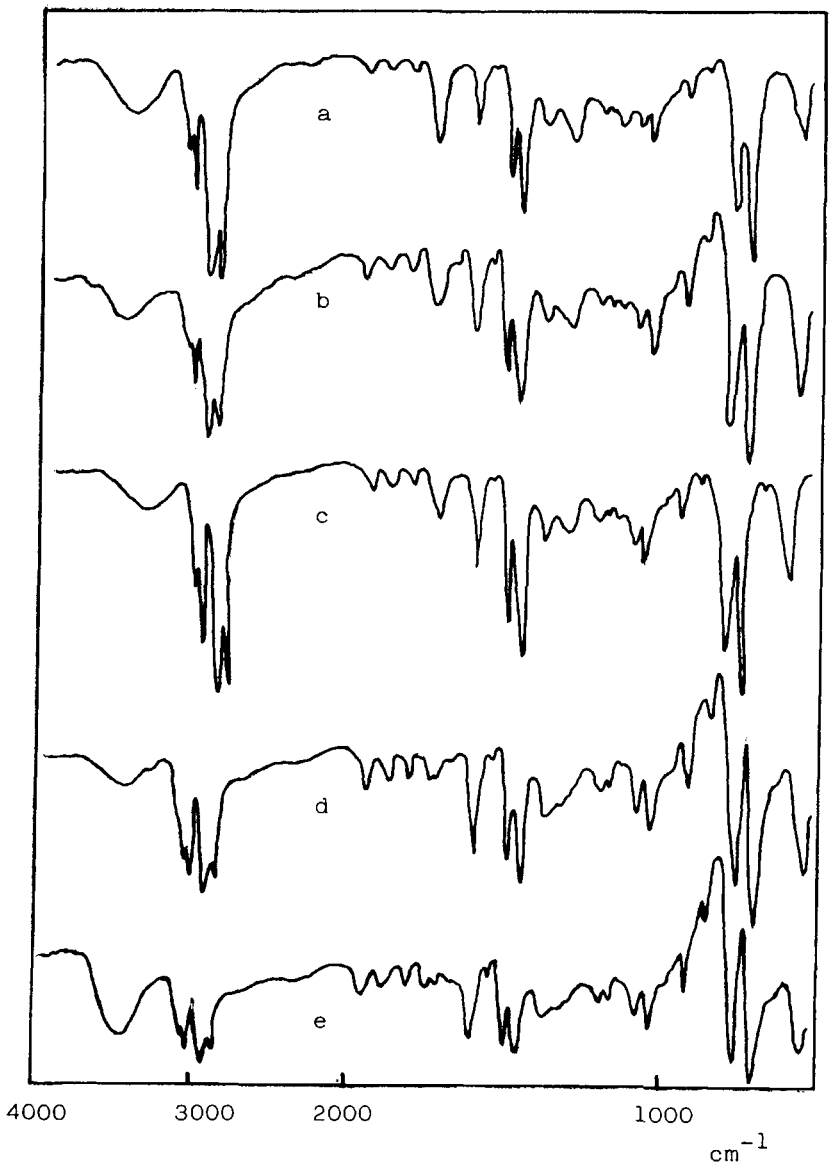


Figure 3 Infrared spectra of graft copolymer after (a) 3, (b) 6, (c) 9, (d) 24, and (e) 32 h of reaction.

The signal at 25.7 ppm can be confirmed by comparing it with the signal at 26.3 ppm related to the methylene group in esters of thioglycolic acid.[8] We could not observe those signals in the sample obtained after 24 h reaction because of the higher percentage of PSty in it.

Attempts were made to quantify the graft copolymerization by ^{13}C-NMR, but the results were not reliable. Therefore, we decided to analyze the PSty grafting efficiency obtained by hydrolysis of the copolymer. Based on the weight of PSty as graft and the values of its molecular weight (M_n), it is possible to determine the average amount of PSty graft and thus the graft efficiency and percent grafting in the copolymer. Table IV describes these values as well the chain transfer constant (Cs) of SH groups located along the trunk copolymer EVAL-SH. The Cs was calculated from the relationship

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

used by Graham and co-workers in their studies envolving graft copolymerization using poly(methyl methacrylate) having a pendant SH group.[7] In this

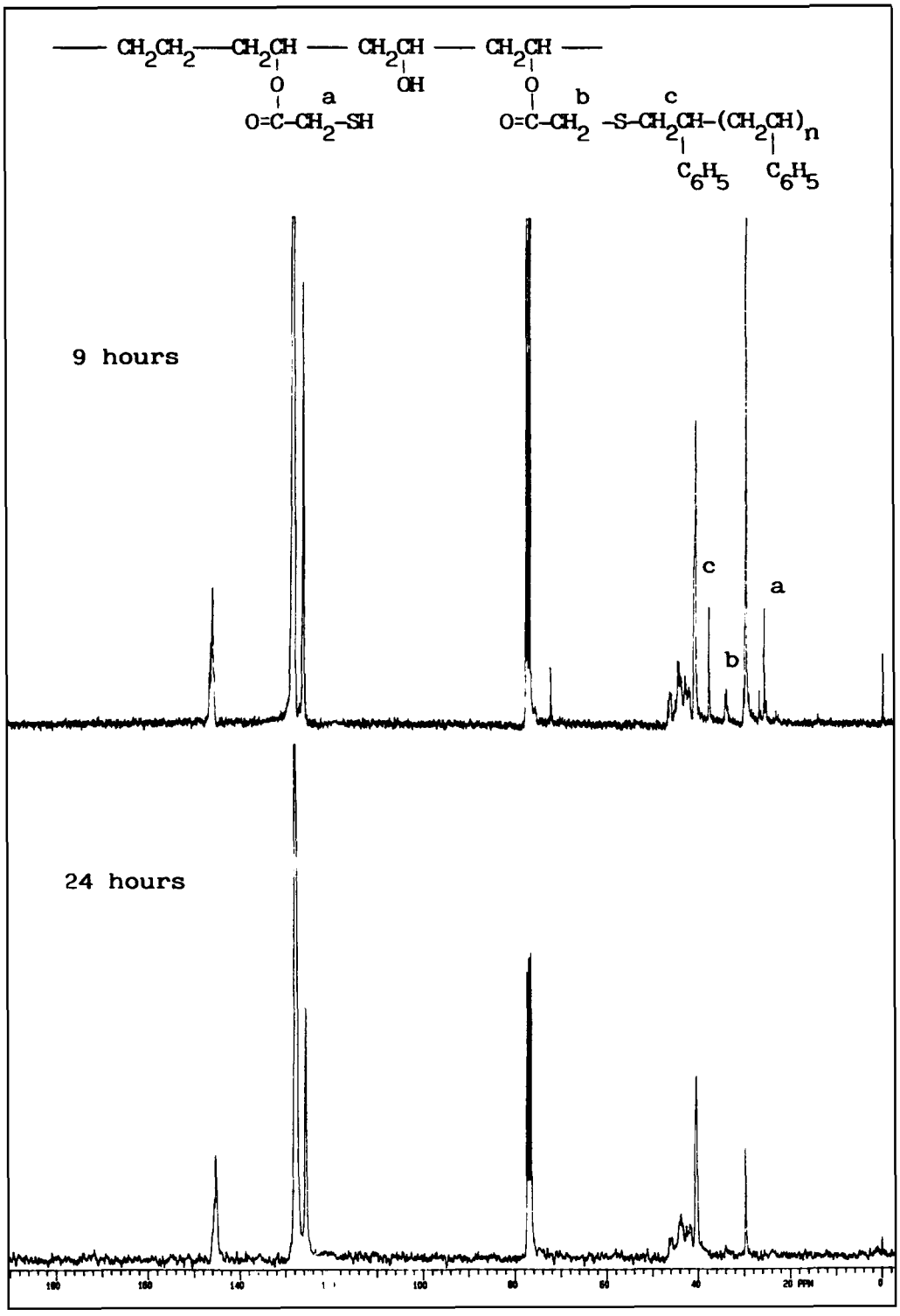


Figure 4 ^{13}C-NMR spectra of the graft copolymers obtained after 9 and 24 h of reaction.

relationship, 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 transfer constant values found in our system are lower than those found in Graham's system and can

be attributed to the lower solubility of EVAL–SH in toluene.

The graft efficiency increases with the time and reaches 49.2% at 32 h of reaction with a 100% conversion of styrene into the polymeric material. The values of graft efficiency is similar to those values reported by Nakamura et al. in graft copolymerization of styrene onto ethylene–vinyl–*p*-nitrobenzoate copolymer.[6] It is worth emphasising that we have employed an $[M]_0/[SH]_0$ ratio about 15 times higher than those used by Nakamura et al. Nevertheless, the system reported in this paper is able to convert 80% of styrene into the graft chain with high molecular weight.

At the moment, we are studying the behavior of these graft copolymers as a compatibilizing agent for PSty with LDPE and EVA and the results will be published soon.

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