# Surface Photografting Polymerization of Vinyl Acetate, Maleic Anhydride, and Their Charge-Transfer Complex. V. Charge-Transfer Complex (1)

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**ABSTRACT:** In previous studies, the photografting polymerization of vinyl acetate (VAC) and maleic anhydride (MAH) was investigated systematically. After that, to increase the grafting rate and efficiency and make the project more practicable, a VAC–MAH binary monomer system was employed for simultaneous photografting onto the surface of low-density polyethylene film. The effects of several crucial factors, including the composition and total concentration of the monomer solution and different types of photoinitiators and solvents, on the grafting polymerization were investigated in detail. The conversion percentage (CP), grafting efficiency (GE), and grafting percentage were measured by gravimetry. The results showed that the monomer composition played a big part in this binary system; appropriately increasing the content of MAH in the monomer feed was suited for grafting polymerization. The growth of the

# INTRODUCTION

Extensive attention has been paid to the surface modification and functionalization of polyolefin substrates, especially since the 1990s, by which targeted products possessing various functional groups and different properties can be prepared. For this purpose, different methods have been developed.<sup>1–3</sup> Among these techniques, photografting polymerization has drawn much attention, mostly because of its obvious advantages, such as low operation cost, mild reaction conditions, selectivity to absorb UV radiation, and relatotal monomer concentration, however, made the copolymerization faster and was unfavorable for grafting polymerization. The three photoinitiators—2,2-dimethoxy-2-phenylacetophenone (Irgacure 651), benzoyl peroxide, and benzophenone (BP)—led to only slight differences in CP, but for GE, BP was the most suitable. As for the different solvents acetone, ethyl acetate, tetrahydrofuran (THF), and chloroform—using those able to donate electrons (acetone and THF) resulted in relatively higher CPs; on the contrary, the use of the other solvents made GE obviously higher, and this should be attributed to the charge-transfer complex (CTC) that formed in this system. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 903–909, 2005

**Key words:** surfaces; photopolymerization; graft copolymers; charge transfer

tively permanent modification effects, without the destruction of the bulk properties of the substrate.

In the literature, the most frequently used monomers for grafting polymerization are acrylic and its derivatives.<sup>4–6</sup> To make the technology of surface photografting polymerization more practicable and less costly but more versatile and environmentally friendly, monomers such as maleic anhydride (MAH) deserve much attention. However, it is widely accepted that MAH cannot homopolymerize under normal conditions<sup>7</sup> but easily participates in copolymerization with other monomers.<sup>8–12</sup> This feature of MAH directs us to apply a binary monomer system, MAH/ vinyl acetate (VAC), to photografting polymerization. Mentioning this kind of copolymerization system, we cannot neglect alternating copolymerization. Despite the fact that many studies have been devoted to it, and progress has been made, some essential points are still open to discussion. That is, the mechanism concerning alternating copolymerization has not been made thoroughly clear. The photografting of such binary monomer systems is a pathway different from that of general methods and will provide better insight into the mechanism of alternating copolymerization.

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TABLE I
Effects of the Monomer Composition on CP (%)

	I (, ,												
Irradiation		[MAH]/[VAC]											
time (s)	0/4	0.5/3.5	1/3	1.5/2.5	2/2	2.5/1.5	3/1	3.5/0.5	4/0				
30	35.3	53.8	68.5	71.0	75.3	77.2	76.2	63.6	36.4				
60	38.7	58.9	70.4	78.4	78.9	86.2	85.2	67.1	48.9				
90	47.3	59.1	77.8	80.2	80.7	87.6	85.9	73.4	72.7				
120	52.3	59.3	81.5	82.5	88.6	88.3	92.3	77.5	75.5				
150	54.0	60.3	86.4	84.3	88.7	88.4	95.4	84.4	88.1				
180	55.3	63.2	87.0	88.5	89.2	94.2	94.6	87.3	85.2				

Irradiation conditions: [MAH + VAC] = 4*M*; intensity of UV radiation = 5500  $\mu$ w/cm<sup>2</sup>; temperature = 30°C; [BP] = 0.2 wt % of the film; solvent = acetone.

In some studies, binary monomer systems were applied to photografting polymerization, but most were carried out in the vapor phase.<sup>13–15</sup> That is, the substrate and MAH and another monomer were placed in a reactor: with heating, the reactor was filled with monomers by vaporization, and some monomer precipitated on the substrate, and with UV-light irradiation, photografting polymerization was started. According to these studies, adding MAH definitely facilitated the photografting polymerization of some monomers, such as styrene and vinyl ethers, but for other monomers, this effect was not obvious. One disadvantage of this technology lies in the fact that photografting polymerization in the vapor phase needs more time, even as much as several hours, even though a higher grafting yield can be obtained. It is thus reasonable to predict that this technology is almost inapplicable for practical use. Furthermore, in these reported studies, because the chance of a chargetransfer complex (CTC) being formed was quite slight, none of these authors mentioned the CTC when they discussed their experimental results.

In our earlier studies, VAC and MAH were successfully photografted onto low-density polyethylene (LDPE) film,<sup>16–19</sup> but for either single monomer, both the grafting rate and grafting efficiency (GE) were actually too low to be industrialized. This article reports investigations of the binary monomer system, and the extension of this work appears to hold great potential for many different applications.

# EXPERIMENTAL

# Materials

LDPE films

Commercial LDPE film samples (63  $\mu$ m thick) were extracted with acetone as a solvent in a Soxhlet's extractor for more than 5 h to eliminate the additives.

# Monomers

Analytically pure MAH (analytical reagent grade), produced by Tianjin Chemical Reagent Plant No. 6 (Tianjin, China), was purified by recrystallization; analytically pure VAC (analytical reagent grade), from Tianjin Tiantai Chemical Reagent Plant (Tianjin, China) was purified by distillation in advance.

# Photoinitiators

Analytically pure 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) from Ciba, chemically pure benzophenone (BP) from Shanghai Reagent Plant No. 1 (Shanghai, China), and analytically pure benzoyl per-

 TABLE II

 Effects of The Monomer Composition on GE (%)

Irradiation		[MAH]/[VAC]									
time (s)	0/4	0.5/3.5	1/3	1.5/2.5	2/2	2.5/1.5	3/1	3.5/0.5	4/0		
30	59.2	69.4	68.7	70.7	78.5	80.9	81.5	65.5	31.3		
60	62.3	70.3	69.9	74.5	82.1	83.6	82.6	65.8	65.1		
90	67.9	75.3	77.8	79.7	82.8	84.8	86.3	74.8	74.3		
120	68.3	75.8	81.6	85.8	84.9	87.8	88.9	79.1	77.3		
150	71.1	76.1	81.8	86.9	88.9	90.4	91.2	81.0	78.9		
180	68.3	75.7	80.9	88.3	90.7	92.1	93.2	80.1	79.1		

Irradiation conditions: [MAH + VAC] = 4*M*; intensity of UV radiation = 5500  $\mu$ w/cm<sup>2</sup>; temperature = 30°C; [BP] = 0.2 wt % of the film; solvent = acetone.



**Figure 1** FTIR spectra of the grafted films: (A) the control LDPE film and (B) the grafted LDPE film.

oxide (BPO) from Jiangsu Hongsheng Chemical Plant (Wuxi, Jiangsu, China) were used as received.

#### Solvents

Acetone, ethyl acetate, tetrahydrofuran (THF), and chloroform (CHCl<sub>3</sub>) were analytically pure grade and were used directly.

#### Grafting procedure

A solution of MAH, VAC and photoinitiator was placed on LDPE films with a microsyringe and distributed evenly with moderate pressure; then, the system was irradiated with UV light for a certain period time (the UV irradiation equipment and the experimental procedure are reported elsewhere in detail<sup>20</sup>). After the irradiation, the films were taken out, separated, and placed in an oven at about 60°C for more than 10 h until a constant weight was obtained to remove the residual monomer. After that, the films were put in a Soxhlet's extractor and extracted with acetone for 8 h to exclude the homopolymers of VAC and MAH and the nongrafted copolymer of VAC and MAH. Finally, the films were dried in the oven to a constant weight again.

The conversion percentage (CP), GE, and grafting percentage (GP) were calculated according to the following definitions:

$$CP = (W_P/W_M) \times 100\%$$
(1)

$$GE = (W_G/W_P) \times 100\%$$
 (2)

$$GP = (W_G/W_F) \times 100\%$$
(3)

where  $W_F$  is the weight of the LDPE films before the grafting polymerization;  $W_M$  is the weight of the added monomers between the two films;  $W_P$  is the weight of the polymer formed, including both the homopolymers of VAC and MAH and the copolymers grafted and not grafted on the LDPE films, obtained by the weighing of the films after the vaporization of the residual monomers; and  $W_G$  is the weight of the grafted polymer, which was obtained after the extraction of the homopolymers and nongrafted copolymers with acetone.

# **RESULTS AND DISCUSSION**

#### Effects of the monomer composition

With the total monomer concentration and other reaction conditions the same, the effects of the monomer composition on the grafting polymerization are shown in Tables I and II. Different monomer compositions had a pronounced influence on the grafting polymerization. In comparison with the grafting polymerizations of both single monomers, that is, VAC and MAH, corresponding to [MAH]/[VAC] ratios of 0/4 and 4/0, the grafting copolymerization of the binary monomer system proceeded more smoothly. Particularly for VAC, the grafting polymerization took place with more difficulty, and this was in good agreement

TABLE III Photografting Polymerization of the MAH–VAC/LDPE System

				0	0 )					5				
[M	+ V] =	2М	[M	+ V] = 3	3М	[M	+ V] =	4M	[M	+ V] =	5M	[M	+ V] = 0	6М
M/T (%)	CP (%)	GE (%)												
0	52.3	68.2	0	41.9	30.0	0	47.6	32.6	0	41.6	18.8	0	57.7	10.0
20	59.3	75.8	16.7	56.4	57.3	20	62.3	46.9	20	58.2	32.6	16.7	80.4	21.9
40	71.5	81.6	33.3	66.9	69.2	40	74.3	54.3	40	77.8	47.6	33.3	90.9	40.2
50	78.6	84.9	50	80.9	80.0	50	85.5	67.2	50	90.9	61.5	50	95.3	53.1
60	82.3	88.9	66.7	87.1	89.3	60	86.6	75.1	60	99.0	69.6	66.7	103.8	69.7
80	85.5	85.1	83.3	87.5	87.2	80	96.5	71.2	80	96.5	60.2	83.3	97.2	41.6
100	71.5	77.3	100	70.7	71.2	100	87.6	55.9	100	90.9	50.1	100	93.3	45.5

M = [MAH]; V = [VAC]; T = [MAH + VAC]. Irradiation conditions: intensity of UV radiation = 5600  $\mu$ W/cm<sup>2</sup>; temperature = 30°C; [BP] 0.2 wt % of the film; irradiation time = 3 min; solvent = acetone.

vent).

with the results already obtained.<sup>20</sup> The results in Tables I and II indicate that photografting copolymerization could be facilitated with the binary monomer system; moreover, both monomers could be grafted onto LDPE films simultaneously, and this was verified

**Figure 2** Effects of the photoinitiators on CP (intensity of the UV radiation =  $5150 \ \mu$ W/cm<sup>2</sup>, irradiation time = 3 min,

temperature =  $45^{\circ}$ C, [MAH] = [VAC] = 2M, acetone = sol-

by Fourier transform infrared (FTIR) spectra (Fig. 1). In comparison with the FTIR spectrum of the control LDPE film, the characteristic absorption peaks of both VAC (1735 cm<sup>-1</sup>) and MAH (1785 cm<sup>-1</sup>) appeared in the FTIR spectra of the grafted film. Therefore, according to these measurements, it could be concluded that both VAC and MAH were grafted onto the substrate because before the measurements, all the residual monomers, homopolymers, and nongrafted copolymers had been completely eliminated with extraction (the composition of the grafted chains will be discussed in another article).

According to Tables I and II, to the binary monomer systems for which [MAH]/[VAC] was 1.5/2.5-3/1, both CP and GE were higher with respect to the other systems, and this showed that these monomer compositions were beneficial for the grafting polymerization, which may be closely related to the CTC formed in the system. It is well known that VAC and MAH can form a CTC that consists of VAC and MAH in a 1/1 ratio.9 For this system, although various CTC equilibrium constants ( $K_{CTC}$ ) have been obtained, such as 0.030 with acetonitrile as a solvent<sup>21</sup> and 0.060 with CHCl<sub>3</sub><sup>9</sup> or dichloroethane<sup>22</sup> as a solvent, it is not doubted that the concentration of CTC in the systems becomes highest when [MAH]/[VAC] is 1/1 with a constant total concentration of MAH and VAC. However, the data in Tables I and II tell us that the highest CP and GE did not appear in the system with a 1/1[MAH]/[VAC] ratio but shifted to the system containing more MAH than VAC (i.e., [MAH]/[VAC] = 2/2-3/1). According to our previous investigations, with UV-light irradiation, a variety of reactions take place simultaneously in this kind of heterophase photografting system, such as the photoreduction of BP, the grafting polymerization of the monomers, hydrogen abstraction by MAH molecule from LDPE films, and subsequent grafting polymerization, the grafting po-

That the highest CP and GE shifted to the system with a bit more MAH than VAC showed that increasing MAH was suited for the photografting polymerization of the binary monomer system to a certain extent. This result should be attributed to a unique feature of MAH: it can abstract hydrogen from LDPE films when irradiated with UV radiation, and this results in the formation of an LDPE macromolecular free radical, which, just like those formed by the photoreduction of BP, can also induce the grafting polymerization of the monomers.<sup>19</sup>

lymerization being initiated by acetone. Therefore, this kind of photografting polymerization seems very

complex.

# Effects of the total monomer concentration

With all other reaction conditions kept unchanged, the effect of the total monomer concentration on the grafting polymerization is described in Table III. Increasing the total monomer concentration, however, led to a markedly increased CP and drastically reduced GE. In other words, the growth of the monomer concentration was unfavorable for enhancing GE of the system. This result may be assigned to the formation of CTC. When the concentrations of both VAC and MAH were increased, the concentration of CTC also went up pro-

**Figure 3** Effects of the photoinitiators on GE (intensity of the UV radiation =  $5150 \mu$ W/cm<sup>2</sup>, irradiation time = 3 min, temperature =  $45^{\circ}$ C, [MAH] = [VAC] = 2*M*, acetone = solvent).







**Figure 4** Effects of the photoinitiators on GP (intensity of the UV radiation =  $5150 \ \mu$ W/cm<sup>2</sup>, irradiation time = 3 min, temperature =  $45^{\circ}$ C, [MAH] = [VAC] = 2M, acetone = solvent).

gressively, and this was more expected for the copolymerization, but not for the grafting copolymerization. In addition, another phenomenon can be observed from Table III: CP exceeded 100%, if calculated according to eq. (1). This outcome was the same as that of MAH; both were due to the participation of a solvent in the copolymerization through the CTC.<sup>23</sup> This point is discussed in detail later. Again from Table III, for the various systems containing the same total concentration of MAH and VAC, an increase in the concentration of MAH facilitated the grafting copolymerization, and this was completely in agreement with the results in Tables I and II.

# Effects of the photoinitiators

The initiation efficiency of three types of photoinitiators (Irgacure 651, BP, and BPO) was assessed in this study. The investigations are shown in Figures 2–4.

Because BPO did not dissolve in acetone smoothly, it was dissolved in CHCl<sub>3</sub> first to prepare a BPO/ CHCl<sub>3</sub> solution, and then a given amount of this solution was added to acetone to prepare MAH, VAC, and BPO/acetone solutions. From the plots displayed in Figures 2–4, it can be clarified that for CP, no obvious difference was observed; but for GE, BP (a Norrish type-II photoinitiator) was better than the other two. Using any of the three photoinitiators could give rise to increased CP and GE, but when no photoinitiator was used, grafting polymerization and nongrafting polymerization still occurred to a certain degree. CP and GE were 60 and 30%, respectively. Two possible pathways could lead to this result. One was initiated by acetone,<sup>4</sup> and the second was initiated by MAH,<sup>19</sup> because both could perform hydrogen abstraction from LDPE macromolecules when irradiated with UV light.

To make it clear, in an extension of our study, as shown in Table IV, in which ethyl acetate was used as the solvent instead of acetone, and no photoinitiator was added to the system, we found that even though no acetone was used, polymerization still took place; however, in comparison with the grafting polymerization in the presence of acetone, both CP and GE dropped; for GE, this phenomenon was more noticeable. The occurrence of photografting polymerization in the absence of a photoinitiator and with ethyl acetate as a solvent was due to initiation by MAH, which was proved already,<sup>19</sup> apart from this, the CTC that formed in this system may have played the same part to a certain degree. It has been reported<sup>24</sup> that in systems containing an electron donor (D) and acceptor (A), such as MAH–VAC, when irradiated by UV light, an exciplex ([D–-A]\*) can be generated as described:

$$D + A \rightarrow [D - A] \xrightarrow{h_V} [D - A]^*$$
 (4)

$$D \longrightarrow D^* + A \rightarrow [D \cdots A]^*$$
(5)

$$A \xrightarrow{h_V} A^* + D \rightarrow [D \cdots A]^*$$
(6)

Photografting Polymerization of VAC/MAH Without a Photoinitiator								
Irradiation time (s)		Ethyl acetate		Acetone				
	CP (%)	GE (%)	GP (%)	CP (%)	GE (%)	GP (%)		
30	47.3	3.8	0.03	59.4	19.5	0.22		
60	54.5	10	0.08	65.5	39.6	0.52		
90	61.8	14.7	0.14	71.6	43.4	0.68		
120	70.9	25.6	0.27	77.8	52.6	0.71		
150	74.5	31.7	0.36	82.1	59.7	0.83		
180	81.8	33.3	0.39	87.8	65.8	0.86		

 TABLE IV

 Photografting Polymerization of VAC/MAH Without a Photoinitiator

Irradiation conditions: temperature =  $45^{\circ}$ C; intensity of UV radiation =  $5150 \ \mu w/cm^2$ ; [MAH] = [VAC] = 2 mol/L.

				0	·			
Irradiation	Acetone		Ethyl acetate		TI	HF	CHCl <sub>3</sub>	
time (s)	CP (%)	GE (%)	CP (%)	GE (%)	CP (%)	GE (%)	CP (%)	GE (%)
30	55.4	44.4	58.2	65.6	81.8	2.2	51.9	50.0
60	64.5	53.6	61.8	70.6	83.6	24.1	58.6	63.6
90	69.9	59.6	69.1	73.7	87.3	31.2	66.3	68.6
120	74.8	68.0	74.5	78.0	92.7	37.2	75.1	76.3
150	80.1	71.2	78.6	79.5	96.4	49.0	78.2	80.1
180	87.5	78 9	81.2	87.8	102.2	56.2	80.5	85.3

 TABLE V

 Effects of the Solvents on the Photografting of the VAC/MAH System

Conditions: temperature = 40°C; UV intensity = 5550  $\mu$ w/cm<sup>2</sup>; [BP] = 0.2 wt % of the film; to solvent CHCl<sub>3</sub>, [VAC] = [MAH] = 1.5*M*; to others, [VAC] = [MAH] = 2*M*.

$$[D - A]^* \rightarrow [\cdot D^+ - A \cdot]$$
(7)

It has been proved that  $[D-A]^*$  is not stable; especially when irradiated by UV radiation, it can transform into  $[\cdot D^+-A \cdot ]$  (reaction 7), which contains two ions and two free radicals simultaneously. Furthermore,  $[\cdot D^+-A \cdot ]$  can undergo hydrogen abstraction in the presence of active hydrogens in the system; this is very similar to MAH.<sup>19</sup> However, to distinguish the contributions of the two cases, extensive work is still needed. Certainly, a chain-transfer reaction may make some contribution to the grafting polymerization also.

# Effects of the solvents

Four agents—ethyl acetate, THF, 2,4-dioxane, and CHCl<sub>3</sub>—were used as solvents. Their influence on the grafting polymerization of the LDPE/VAC–MAH system is presented in Table V. Those solvents able to form CTCs with MAH (Table VI), such as THF and dioxane, led to higher CPs, but those not able to form CTCs with MAH, that is, ethyl acetate and CHCl<sub>3</sub>, gave rise to relatively higher GEs. All these characteristics were similar to those of the photografting polymerization of MAH in solution.<sup>23</sup> Different solvents not only affected the values of CP and GE but also led to different distributions of grafted chains on LDPE films. Consider, for example, ethyl acetate and CHCl<sub>3</sub>. The differences in the distributions of the grafted

chains were shown clearly by attenuated total reflection/infrared (ATR-IR) spectra (Fig. 5).

From Figure 5, the characteristic absorption peak areas of LDPE (2915 cm<sup>-1</sup>), poly(VAC) (1735 cm<sup>-1</sup>), and poly(MAH) (1785 cm<sup>-1</sup>) were calculated with the following method. All the spectra were recorded on the same type of paper. The part of the paper enclosed by each absorption peak was cut along with the peak line, and the paper sheets were weighed. The weights of the paper sheets were taken as the areas of the corresponding peaks. The results are listed in Table VII.

On the basis of Figure 5 and Table VII, both  $A_{VAC}$  $A_{\text{LDPE}}$  and  $A_{\text{MAH}}/A_{\text{LDPE}}$  (where  $A_{\text{VAC}}$ ,  $A_{\text{MAH}}$ , and  $A_{\rm LDPE}$  are the characteristic absorption peak areas of VAC, MAH, and LDPE, respectively), with ethyl acetate as a solvent, were lower than those with CHCl<sub>3</sub> as a solvent, even though their GPs were nearly the same. This showed that more grafted chains with ethyl acetate as a solvent were located near the surface of the LDPE film, in comparison with those when CHCl<sub>3</sub> was used as the solvent. This result seems to be due to the different affinities between the solvents and LDPE films. Although the solubility parameter (SP) of ethyl acetate was 9.1, closer to the SP of LDPE films (SP = 7.9) than that of CHCl<sub>3</sub> (SP = 9.4),<sup>17</sup> CHCl<sub>3</sub> diffused far more easily on LDPE films than ethyl acetate did. Therefore, the affinity between CHCl<sub>3</sub> and LDPE was higher than that between ethyl acetate and

TABLE VIK<sub>CTC</sub> of Agent/MAH Systems

		•			
$\varepsilon^{a}$	Solvent	Temperature (°C)	Method	K <sub>CTC</sub>	Reference
20.7	<i>n</i> -Hexane	25	UV	0.79	25
	<i>n</i> -Hexane	30	NMR	0.667	26
	CHCl <sub>3</sub>	25	UV	0.75	27
4.806	Cyclohexane	60	NMR	0	27
6.02	·		_	_	_
7.58	<i>n</i> -Hexane	30	NMR	0.44	26
	ε <sup>a</sup> 20.7 4.806 6.02 7.58	$\begin{array}{c c} \varepsilon^{a} & Solvent \\ \hline 20.7 & n-Hexane \\ & n-Hexane \\ & CHCl_{3} \\ 4.806 & Cyclohexane \\ 6.02 & \\ 7.58 & n-Hexane \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

<sup>a</sup> Dielectric constant.

<sup>b</sup> It is generally accepted that it cannot form CTC with MAH.

LDPE. The higher the affinity was, the more deeply the grafted chains were distributed on the substrate, and this certainly led to lower values of both  $A_{VAC}/A_{LDPE}$  and  $A_{MAH}/A_{LDPE}$ . In other words, when agents are chosen as the solvents of VAC and MAH for photografting polymerizations, not only is the ability of the solvent to donate electrons to MAH to form CTCs worthy of attention, but the affinity between the solvent and LDPE film should not be neglected.

# CONCLUSIONS

Both VAC and MAH were grafted onto LDPE films with the binary monomer system, and the photografting polymerization of the binary monomer system proceeded more easily than the photografting polymerization of either monomer by itself. The monomer composition, the total monomer concentration, and the type of photoinitiator had a great influence on the grafting polymerization; meanwhile, different solvents not only had different effects on the grafting polymerization but also affected the distribution of the grafted chains on the substrate.



**Figure 5** ATR–IR spectra of the LDPE films: (A) blank LDPE film, (B) grafted film (GP = 0.50%, solvent = CHCl<sub>3</sub>), and (C) grafted film (GP = 0.48%, solvent = ethyl acetate).

TABLE VII Ratios of Peak Areas from ATR–IR Spectra

Film sample	GP (%)	$A_{\rm VAC}/A_{\rm LDPE}$ (%)	A <sub>MAH</sub> /A <sub>LDPE</sub> (%)	Solvent
B	0.50	16.71	12.12	CHCl <sub>3</sub>
C	0.48	37.50	31.11	Ethyl acetate

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