# Styrene-Assisted Melt Free Radical Grafting of Glycidyl Methacrylate onto an Ethylene and Propylene Rubber

### **GUO-HUA HU, HERVÉ CARTIER**

Laboratoire d'Extrusion Réactive, ECPM—Département Polymères, Institut Charles Sadron, 4 rue Boussingault, 67000 Strasbourg, France

Received 25 February 1998; accepted 31 May 1998

ABSTRACT: This article deals with the efficiency of using styrene (St) as a comonomer to promote the melt free radical grafting of glycidyl methacrylate (GMA) onto an ethylene and propylene rubber (EPR) in a batch mixer and a corotating self-wiping twin screw extruder. The addition of St to an EPR/GMA/peroxide system increases not only GMA's grafting yield but also its grafting rate. The time required for the EPR/GMA/peroxide system without St to reach a given amount of grafted GMA is at least 10 times that needed for the same system in the presence of an equimolar amount of St. For example, about 60 min are required for the EPR/GMA/dicumyl peroxide (composition: 100/3.0/0.3 by weight) to reach 1.5 phr (parts per hundred resin) GMA (i.e., 1.5 g grafted GMA per 100 g EPR). The same amount of grafted GMA is reached in < 3 min when 3.0 phr St is charged to the system. This significant reduction of reaction time is crucial for a successful free radical grafting of GMA on EPR in a corotating twin screw extruder, because the residence time in such a machine is typically on the order of 0.5–5 min. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 125–133, 1999

**Key words:** reactive extrusion; free radical grafting; glycidyl methacrylate; ethylene and propylene rubber; styrene

# INTRODUCTION

During the last decade, a sizable amount of effort has been made to free radically graft functional monomers onto elastomers such as copolymers of ethylene and propylene rubber (EPR), copolymers of ethylene, propylene and diene (EPDM), and copolymers of styrene, ethylene, butylene, and styrene (SEBS).<sup>1–9</sup> Among functional monomers tested, maleic anhydride received most of the attention because of its widespread applications for toughening polyamides. Maleic anhydride–modified elastomers are capable of reacting with the amine terminal group of polyamides leading to the *in situ* formation of amphiphilic copolymers at the interfaces between elastomers and polyamide.<sup>10</sup>

Glycidyl methacrylate (GMA) is another interesting monomer owing to its epoxy group, which is capable of reacting with various other groups like hydroxyl, carboxyl, amine, and anhydride. For example, GMA-modified EPR was used to toughen poly(butylene terephthalate).<sup>11</sup> More recently, GMA chemistry was successfully used to compatibilize polyolefin and polyester blends.<sup>12–15</sup>

However, the melt free radical grafting reactivity of GMA toward saturated hydrocarbon polymer backbones is low. For example, the conversion of GMA to grafted species is typically below 10% for polypropylene (PP) and 20% for polyethylene (PE).<sup>16,17</sup> Recently, a so-called "comonomer concept" was developed to improve GMA's grafting yield onto PP and PE.<sup>16–20</sup> The idea of using a

*Correspondence to:* Guo-Hua Hu. As of September 1, 1998, Professor at the Institute National Polytechnique de Lorraine (INPL), NANCY, FRANCE

Journal of Applied Polymer Science, Vol. 71, 125-133 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/010125-09

Abbreviation	Chemical Structure	Rate of Decomposition		
DCP	$\left\langle \bigcirc \right\rangle \begin{array}{c} \overset{\mathrm{CH}_{3}}{\underset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\underset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\underset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\underset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{\mathrm{CH}_{3}}}{\overset{CH}_{3}}}{\overset$	$K_d = 9.2  imes 10^{15}  (-18  350/T)  ({ m s}^{-1})$		
DTBPIB	$t-C_4H_9-OO-C_C_{I_1}$ $CH_3$ $CH_3$ $I_2$ $OO-t-C_4H_9$ $CH_3$ $CH_3$	$K_d = 7.7  imes 10^{15} (-18\ 350/T)  ({ m s}^{-1})$		

	Table I	Rates of <b>D</b>	<b>Decomposition</b>	of the	Peroxides	Used i	in this	Study
--	---------	-------------------	----------------------	--------	-----------	--------	---------	-------

second monomer or a comonomer is associated with the commonly accepted fact that a free radical process starts with the formation of macroradicals along the polymer chains by a so-called hydrogen abstraction mechanism. These macroradicals may subsequently follow two competing pathways. They can either initiate the grafting of the monomer (which is desirable) or undergo chain branching, crosslinking, and/or scission (which is often undesirable). This latter depends very much on the nature of the polymer backbone. In the case of PP, the main side reaction is  $\beta$ -scission associated with PP tertiary macroradicals, which causes a reduction in the molecular weight of the polymer. In the case of PE, the main side reaction is crosslinking as a result of the recombination of secondary macroradical. To obtain high grafting yields with reduced side reactions, it is essential that the macroradicals react with the grafting monomer before they undergo side reactions. Because GMA is not very reactive toward PP tertiary macroradicals or PE secondary macroradicals, it would be helpful to use a second monomer that can react with them much faster than GMA and the resulting macroradicals can then copolymerize readily with GMA. In this way, instead of grafting GMA directly onto PP or PE chains, the comonomer serves as a mediator to bridge the gap between the PP or PE macroradicals and GMA monomer. Styrene (St) was found to be a good comonomer to promote the melt free radical grafting of GMA onto PP and PE. This was believed to be related to the fact that St reacts rapidly with PP or PE macroradicals and the resulting styryl macroradicals copolymerize readily with GMA monomer.

The aim of this study is to investigate the melt free radical grafting of GMA onto EPR in a batch mixer and in a corotating self-wiping twin screw extruder. Considering the chemical structure of EPR, which is a random arrangement of ethylene and propylene moieties, the melt free radical grafting of GMA onto EPR will likely face similar problems as those mentioned above for PP and PE. It will be shown that they can be solved with the comonomer concept. The melt free radical grafting of GMA onto a mixture of EPR and PP will also be discussed.

### **EXPERIMENTAL**

#### **Materials**

The EPR used in this study was kindly supplied by Exxon Chemicals Europe, Belgium (Vistalon 805). It contained 77 wt % ethylene moieties and had a melt flow index of 5 g/10 min at 230°C/10 kg. The PP was obtained from Montell, Belgium (Valtec CL101D). The PP melt flow index was 0.3 g/10 min at 230°C/2.16 kg; its number and weight average molecular weights were 141 000 and 645 000 g/mol, respectively. It was in the form of porous pellets capable of absorbing liquid reagents. St and GMA were purchased from Aldrich and used as received. Two different commercial peroxides from Akzo (France) were used:  $\alpha, \alpha'$ di(t-butyl-peroxy)-1,3- and 1,4-diisopropylbenzene (DTBPIB) and dicumylperoxide (DCP). Their rates of decomposition are shown in Table I.

#### **Experimental Procedures**

Free radical grafting experiments were carried out in a Rheocord Haake (Karlsruhe, Germany) batch mixer (50 cm<sup>3</sup>) and in a twin screw extruder. For a typical grafting experiment in the batch mixer, the EPR (40 g) was first charged to the preheated mix-



**Figure 1** Screw profile, the monomer injection locations, and the sampling ports used in this study. The monomers and peroxide were injected at Port 1 after the first kneading zone and samples were taken at port 2 and the die exit.

ing chamber. After the torque of the molten EPR was stabilized, the liquid reactants (GMA, St, and peroxide) were added. In the case of GMA's grafting onto a mixture of EPR and PP (50/50 by weight), the liquid reagents were premixed with the PP porous pellets before being charged to the molten EPR. For kinetic studies, samples were taken out of the mixing chamber quickly and then quenched immediately into liquid nitrogen to stop the reaction.

The twin screw extruder used in this study was a corotating self-wiping twin screw extruder of type Werner & Pfleiderer ZSK-30. The screw diameter (D) was 30.8 mm and the screw diameterto-extruder length ratio excluding the die was 42. This type of machine has a great flexibility in terms of screw and barrel, as well as temperature profiles, due to its modular character. In practice, it is often starved fed. In other words, unlike in a single screw extruder in which the throughput is determined by its pumping capacity, which in turn is related to screw speed, the throughput in this type of twin screw extruder is an independent processing parameter which can be chosen "at will" as long as it is smaller than the pumping capability of the machine in question. The screw profile, the monomer injection locations, and sampling ports used in this study are shown in Figure 1.

The EPR was fed to the extruder using a weight loss screw feeder of type K-Tron K10S. A mixture of GMA (and/or St) and peroxide was added to the molten EPR at Port 1 just after the first kneading zone in which the EPR became plastified. The injection was done with a gel permeation chromatography (GPC) pump that could operate under high pressures (up to 80 bars) and had a capacity of between 0.1 and 5.0 mL/min. A second GPC pump was used for higher flow rates (between 4 and 30 mL/min). To follow up the evolution of GMA's grafting along the screw length, samples were taken out at port 2 and the

die exit, and then cooled immediately in liquid nitrogen to stop the reaction. Residual monomers were removed from a venting port with a vacuum pump. All experiments were carried out under a nitrogen purge at the hopper to minimize oxidation.

# Determination of the Amount of Grafted GMA onto EPR or a Mixture of EPR and PP

The procedures used for purifying GMA-modified EPR samples were the same as those described elsewhere.<sup>16,17</sup> Basically, they were dissolved in boiling xylene and precipitated in acetone to remove unreacted and polymerized GMA. They were then dried in a vacuum oven overnight at 80°C. Grafting yields were determined by Fourier transform infrared spectroscopy (FTIR). The peak at  $1304 \text{ cm}^{-1}$  was chosen as the internal reference of the EPR and the one at  $1736 \text{ cm}^{-1}$  as the target for determining the amount of grafted GMA. The calibration curve was established with GMAmodified EPR samples from which GMA grafting yields were measured separately by elemental analysis and/or <sup>1</sup>H-NMR (see Fig. 2). For a mixture of EPR and PP, GMA's grafting yield onto each of the two polymers was measured by first separating EPR and PP by selective dissolution of the EPR in cyclohexane at room temperature in which the PP remained insoluble. This technique worked quite satisfactorily because the same results were obtained using xylene as a selective solvent for dissolving EPR at 70°C. GMA's grafting yields onto PP were also measured by FTIR according to the procedures described elsewhere.16,18

# **RESULTS AND DISCUSSION**

Early studies  $^{16-20}$  showed that the addition of St as a comonomer to the PP/GMA/peroxide or PE/



**Figure 2** IR calibration curve for measuring GMA's grafting yield onto EPR.

GMA/peroxide system increased both GMA's grafting yield and grafting rate. The proposed mechanism of the St-assisted free radical grafting was that St reacted first with PP tertiary macroradicals or PE secondary macroradicals and the resulting styryl macroradicals then copolymerized with GMA. In this way, instead of grafting GMA directly onto PP or PE chains, the comonomer served as a mediator to bridge the gap between the PP or PE macroradicals and GMA monomer. This is depicted in Figure 3.

An EPR is composed of ethylene and propylene moieties more or less randomly distributed along the chain. Thus, the use of St as a comonomer for the EPR/GMA/peroxide system should also be beneficial. This will be confirmed in the next section.

### EPR Molecular Structure Change During the Free Radical Grafting

Besides the desired grafting, side reactions are always an important issue of any free radical grafting process. In the case of EPR, there exist secondary and tertiary macroradicals. Secondary macroradicals tend to recombine leading to chain branching and/or crosslinking, as is the case for PE. On the other hand, tertiary macroradicals are prone to chain degradation by  $\beta$ -scission, as is the case for PP. Hence the molecular change of EPR is expected to be somewhere in between, depending, among other things, on the molar ratio between ethylene and propylene moieties in the copolymer. This ratio was about 5 for the EPR used in this study (i.e., 1 propylene unit per every 5 ethylene units).

For the grafting experiments carried out in the batch mixer, the evolution of the torque during the grafting process gives a rough idea about the evolution of the viscosity of the EPR, thus its molecular change. The torque histogram for the virgin EPR and the EPR/GMA/DCP system at 175°C is shown in Figure 4. The torque of the virgin EPR started to decrease after 5 min of mixing. This suggests that the EPR had probably undergone thermally induced chain degradation. The situation was quite different for the EPR/ GMA/DCP system. In this case, the torque decreased slightly during mixing. Apparently, branching and/or crosslinking of the ethylene part of the EPR chains recompensed for the chain scission of the propylene part.



**Figure 3** Schematic description of styrene-assisted free radical grafting of GMA onto PP and PE.



**Figure 4** Torque and the real melt temperature as a function of time for a targeted melt temperature of  $175^{\circ}$ C. (——): EPR; ( $\bigcirc$ ): EPR + 3.0 phr GMA + 0.3 phr DCP.

The thermally induced EPR chain degradation became almost insignificant when the melt temperature was lower. For example, at 155°C the torque of the virgin EPR remained constant for 20 min (see Fig. 5). Also, the difference in terms of torque was small between the virgin and two reacting systems (EPR/GMA/DCP and EPR/GMA + St/DCP). This implies that it would be preferable to carry out the free radical grafting at low temperatures so as not to alter the molecular characteristics and related properties of the EPR.



**Figure 5** Torque and real melt temperature as a function of time for a targeted melt temperature of  $155^{\circ}$ C. (——): EPR; ( $\bigcirc$ ): EPR + 3.0 phr GMA + 0.3 phr DCP; ( $\triangle$ ): EPR + 3.0 phr GMA + 3.0 phr St + 0.3 phr DCP.



**Figure 6** Effect of adding St on the grafting of GMA onto EPR.  $[GMA]_i = 3.0 \text{ phr}; [DCP]_i = 0.3 \text{ phr}; [St]_i/[GMA]_i = 0 (without St) or 1.0 mol/mol (with St). Mixing speed = 64 rpm (revolutions per minute).$ 

#### Effects of St on GMA's Grafting onto EPR

Figure 6 shows GMA's grafting yield as a function of reaction time with or without St at various reaction temperatures using DCP as a free radical generator. In the absence of St, GMA's grafting yield increased gradually with increasing reaction time during the whole grafting process (between 0 and 45 min). An increase in reaction temperature seemed to speed up the grafting rate.

When St was added to the EPR/GMA grafting system, GMA's grafting behaved differently. GMA's ultimate grafting yields were much higher and the grafting proceeded much faster. The grafting was close to completion after 15 min of reaction. GMA's grafting yield obtained after 15 min of reaction at 175°C in the presence of St is three times higher than that obtained in the absence of St under otherwise the same reaction conditions. The conversion of the GMA monomer to grafted species was more than 80%.

The great difference in GMA's grafting rate between the EPR/GMA/peroxide and EPR/GMA + St/peroxide systems deserves further comment. Considering the fact that the presence of St in the EPR/GMA/DCP system should not alter much the rate of decomposition of DCP, a greater grafting rate with St implies that the rate of GMA's free radical grafting onto EPR is not controlled by the rate of decomposition of the peroxide (DCP), but rather by the reaction rate between GMA and EPR macroradicals in the EPR/GMA/DCP system or between St and EPR macroradicals in the EPR/GMA + St/DCP system.

The effect of St on GMA's grafting yield increase is also illustrated in Figure 7, in which GMA's grafting yield is plotted as a function of GMA's initial concentration. When St was added to the EPR/GMA/DCP system, GMA's grafting yields were much higher. This was especially true for high initial GMA concentrations. In the absence of St, GMA's grafting yield tended to level off at high initial GMA concentrations. The conversion of GMA to grafted species decreased accordingly from  $\sim$  70 to 20% when GMA's initial concentration was increased from 1 to 6 phr. On the other hand, when St was added, GMA's grafting yield increased almost linearly with increasing GMA initial concentration. Its conversion decreased slightly with increasing GMA initial concentration as it went from  $\sim 80$  to 60% when GMA's initial concentration was increased from 1 to 6 phr.

# Effect of the Nature of and Concentration of Peroxide on GMA's Grafting Yield

Figure 8 compares GMA's grafting yield between two free radical initiators, DCP and DT-BPIB. The grafting efficiency of DCP was somewhat higher than that of DTBPIB. However, the



Figure 7 Effect of adding St on GMA's grafting yield and conversion as a function of its initial concentration.  $[DCP]_i = 0.3$  phr; temperature = 155°C; reaction time = 20 minutes. ( $\bigcirc$ ): EPR/GMA/DCP system; ( $\bigcirc$ ): EPR/GMA + St/DCP system ( $[St]_i/[GMA]_i = 1.0 \text{ mol/mol}$ ).



**Figure 8** Effect of the peroxide concentration on GMA's grafting yield onto EPR.  $[GMA]_i = 3.0$  phr;  $[St]_i/[GMA]_i = 0$  or 1 mol/mol; temperature = 155°C; reaction time = 20 minutes.

reasons for this difference are not clear. Apparently, it is not related to the rate of decomposition of the peroxide, because it is supposed to be similar for both peroxides. It might be that they generate different primary radicals that do not necessarily have the same reactivity. Also, on an equal weight basis, the molar concentration of DCP is higher than that of DTBPIB. In any event, for both peroxides, GMA's grafting yield increased with increasing peroxide concentration. However, this increase tended to level off at high peroxide concentrations. In fact, appreciable GMA's grafting yields were obtained with only 0.1 phr peroxide. This was particularly true when St was present. Since the molar ratio between grafted species and primary free radicals was much higher than one, namely, one primary free radical yielded more than one GMA and/or St grafted species, the regeneration of macroradicals by hydrogen transfer along the EPR chains might have been important. It should be noted, however, that GMA's grafting yield was low ( $\sim 0.1$  phr) without external free radical generator, implying that thermal oxidation-induced GMA grafting was unimportant for the EPR/GMA/DCP system. On the other hand, when St was added, GMA's grafting yield was increased to about 0.5 phr in the absence of an externally added free radical generator.



**Figure 9** Grafting of GMA onto a mixture of EPR and PP (50/50 by weight) in the presence of styrene.  $[GMA]_i$  = 3.0 phr;  $[St]_i/[GMA]_i = 1.0 \text{ mol/mol}$ ;  $[DCP]_i = 0.3 \text{ phr}$ ; temperature = 180°C.

#### Grafting of GMA onto a Mixture of EPR/PP (50/50)

Figure 9 shows the evolution of GMA's grafting yield as a function of time for a mixture of EPR and PP at 180°C in the presence of St. Such a functionalized system could have specific applications. GMA's grafting yield onto EPR was slightly higher than that onto PP, 0.85 and 0.98 phr for PP and EPR, respectively. The grafting proceeded equally fast for both polymers and was completed within 2 min of reaction.

For a given initial concentration of GMA, its grafting yield could vary to a great extent, depending on the amount of St added, shown in Figure 10. When the initial concentration of GMA was 3.0 phr, the grafting yield onto EPR ranged from 0.54 to 1.42 phr when  $[St]_{i}/[GMA]_{i}$  varied from 0 to 2 mol/mol. Similarly, GMA's grafting yield onto PP ranged from 0.39 to 0.97 phr.



**Figure 10** GMA's grafting yield onto a mixture of EPR and PP (50/50 by weight) as a function of  $[St]_i/[GMA]_i$  for a given amount of GMA (3.0 phr). Temperature =  $180^{\circ}$ C;  $[GMA]_i = 3.0$  phr;  $[DCP]_i = 0.3$  phr.

#### Grafting of GMA in a Corotating Twin Screw Extruder

Table II shows the effects of the barrel temperature and the presence of St on GMA's grafting yield of the EPR/GMA/DCP system with and without St. Similar to the results obtained in the batch mixer, both barrel temperature and the presence of St were important for GMA's grafting yield. Without St, it was 1.3 phr at 200°C and 0.2 phr at 150°C. In the presence of St, it was increased to 2.2 phr at 200°C and 1.4 phr at 150°C.

GMA's grafting proceeded rapidly in the twin screw extruder because GMA's grafting yield at Port 2 was not different from that at the die exit, irrespective of the barrel temperature and/or the presence of St. The mean residence time between port 1 (injection of GMA) and port 2 was esti-

 Table II
 Effects of Barrel Temperature and the Presence of St on GMA's Grafting Yield along the

 Screw Length

Reference	Temperature (°C)	[GMA] <sub>i</sub> (phr)	[St] <sub>i</sub> (phr)	[DCP] <sub>i</sub> (phr)	[GMA] <sub>g</sub> (phr) at Port 2	[GMA] <sub>g</sub> (phr) at the Die Exit
А	200	3.0	3.0	0.3	2.1	2.2
В	200	3.0	_	0.3	1.4	1.3
С	150	3.0	3.0	0.3	1.2	1.4
D	150	3.0	—	0.3	0.2	0.2

Throughput, 3.0 kg/h; screw speed, 100 rpm.



**Figure 11** Viscosity as a function of shear rate for the virgin EPR and GMA-modified EPR samples. ( $\Box$ ): EPR; ( $\nabla$ ): GMA modified EPR (B in table 2); ( $\bigcirc$ ): GMA-modified EPR (C in table 2); ( $\triangle$ ): GMA modified EPR (C in table 2).

mated to be < 30 sec. It is, however, somewhat surprising that the EPR/GMA/peroxide system without St had already gone to completion at port 2, considering the fact that the free radical grafting of the grafting rate of EPR/GMA/peroxide system without St is relatively slow in the batch mixer (see Fig. 5).

Figure 11 compares the viscosity of the virgin EPR and that of the GMA-modified EPR samples under the conditions specified in Table II. All GMA-modified EPR samples had almost the same viscosity, which was also very close to that of the virgin EPR. This suggests that the molecular structure of EPR was not significantly affected by the grafting. This was further supported by the following two experimental facts: (1) all GMAmodified EPR samples were soluble in hot xylene and (2) their glass transition temperatures were the same as that of the virgin EPR. This latter fact is very important because the glass transition of elastomers dictates, to a great extent, its toughening efficiency.

It is also interesting to note that unlike GMA, maleic anhydride (MA) has a great tendency to crosslink EPR. For example, when MA was grafted onto EPR under the same conditions as those in Table II, all the modified EPR samples were more or less crosslinked and only partly soluble in hot xylene. This is in agreement with the observation that their viscosity was higher than that of the virgin EPR. Separate studies showed that MA caused more PP chain degradation and PE chain crosslinking than GMA. The question remains why GMA and MA behave so differently. One possible explanation would be that the reactivity of MA free radical toward a hydrogen atom could be greater than that of GMA free radical. Once MA is grafted onto a hydrocarbon substrate, it will transfer its free radical to a carbon atom of the substrate by abstracting a hydrogen atom from it. This will lead subsequently to chain degradation when the hydrocarbon substrate is PP or chain crosslinking when the substrate is PE.

### CONCLUSION

In this article, it was shown that St is a good comonomer to promote the melt free radical grafting of GMA onto an EPR. The addition of St to an EPR/GMA/peroxide system increases not only GMA's grafting yield but also its grafting rate. To reach a given GMA's grafting yield, the time required for the EPR/GMA/peroxide system in the presence of St is only one-tenth of what it would take without St. An increase in temperature favors GMA's grafting yield and rate but may cause more EPR degradation. The significant reduction in reaction time as a result of adding St is crucial for a successful free radical grafting of GMA on EPR in a corotating twin screw extruder, because the residence time in such a machine is often limited to  $\sim$  1–5 min. Comparative studies have shown that unlike GMA, MA has a great tendency to cause EPR crosslinking. The reasons for this are unknown.

The authors are grateful to Borealis, Norway, for their financial support and to Ms. Hélène Doucet and Ms. Sabine Boillod for their contributions to this work during their training in our laboratory.

### REFERENCES

- Wu, C. H.; Su, A. C. Polym Eng Sci 1991, 31, 1629.
- Coran, A. Y.; Patel, R. P. Reactive Modifiers for Polymers, S. Al-Malaika, Ed., Thomson Science & Professional: London, 1997, Chap. 9.
- Greco, R.; Maglio, G.; Musto, P. J Appl Polym Sci 1987, 33, 2513.

- Greco, R.; Musto, P.; Riva, F.; Maglio, G. J Appl Polym Sci 1989, 37, 789.
- Oostenbrink, A. J.; Gaymans, R. J. Polymer 1992, 33, 14.
- Gaylord, N. G.; Metha, M.; Metha, R. J Appl Polym Sci 1987, 33, 2549.
- 8. Hogt, A. J. in Proceedings COMPALLOY 90, New Orleans, 1990.
- 9. Hu, G. H.; Flat, J. J.; Lambla, M. Makromol Chem Macromol Symp 1993, 75, 137.
- Gonzalez-Montiel, A.; Keskkula, H.; Paul, D. R. Polymer 1995, 36, 4587.
- Moffett, A. J.; Dekkers, M. E. J. Polym Eng Sci 1992, 32, 1.
- 12. Hu, G. H.; Sun, Y. J.; Lambla, M. Polym Eng & Sci 1996, 36, 676.

- Hu, G. H.; Sun, Y. J.; Lambla, M. J Appl Polym Sci 1996, 61, 1039.
- Sun, Y. J.; Hu, G. H.; Lambla, M.; Kotlar, H. K. Polymer 1996, 37, 4119.
- 15. Cartier, H. Ph.D. dissertation, Université Louis Pasteur de Strasbourg, France, 1997.
- Sun, Y. J.; Hu, G. H.; Lambla, M. Angew Makromol Chem 1995, 229, 1.
- Sun, Y. J.; Hu, G. H.; Lambla, M. J Appl Polym Sci 1995, 57, 1043.
- Cartier, H.; Hu, G. H. J Polym Sci, Part A: Chem Ed 1998, 36, 1053.
- Hu, G. H.; Flat, J. J.; Lambla, M. (pages 1-80) in Reactive Modifiers for Polymers, S. Al-Malaika, Ed., Thomson Science & Professional: London 1997, Chapter 1.
- 20. Cartier, H.; Hu, G. H. Polym Eng Sci, to appear.