

Influence of Styrene on Grafting Efficiency of Maleic Anhydride onto Natural Rubber

J. Saelao,^{1,2} P. Phinyocheep^{1,2}

¹Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Phayathai, Bangkok 10400, Thailand

²Institute of Science and Technology for Research and Development, Salaya Campus, Mahidol University, Nakorn Pathom 73170, Thailand

Received 16 October 2003; accepted 14 April 2004

DOI 10.1002/app.20810

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Grafting of maleic anhydride (MA) onto natural rubber (NR) has been investigated by using a radical initiated grafting process. NR was masticated to lower molecular weight than the original NR before treatment with 0.5–1.5% by mole of benzoyl peroxide (BPO) and 5–25% by mole of MA in toluene solution. Fourier transform infrared spectroscopy (FTIR) and titration method were used to analyze the fixation of MA on the NR. The reaction temperature was varied from 60 to 80°C. The % grafting of MA was

higher at higher temperatures. Compared to the reaction without styrene, the addition of 0.1% by mole of styrene in the grafting process increased % MA grafting up to two times. It is postulated that the styrene may act as a charge transfer complex for the reaction of NR with MA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 28–38, 2005

Key words: charge transfer; FTIR; maleic anhydride; modification; rubber

INTRODUCTION

Maleic anhydride (MA) is one of the most widely used vinyl monomers for the graft modification of polyolefin, including PE, PP, PS, EPR, and EPDM.^{1–11} Introduction of MA on the nonpolar backbone of polyolefin has overcome the disadvantage of low surface energy of the polyolefin. This not only improves the hydrophilicity of the surface of the polyolefins for the benefit of printing and coating applications but also the adhesion of the polyolefins with polar polymers such as polyamide, metal, and glass fibers. MA-modified polyolefins are also used as impact modifiers and compatibilizer in polymer blends.^{12,13} Natural rubber (NR) is widely used in various applications particularly for tires because of its excellent elastic properties over other synthetic counterparts. However, its nonpolar character limits its application due to poor oil resistance and high air permeability. Graft copolymerization with MA or other polar monomers can introduce polar groups on the nonpolar NR backbone. This improves the compatibility between NR and other polar elastomers and some engineering plastics such as polyamide.^{14,15}

Most of the studies of MA grafting onto polyolefins have involved the free radical grafting mechanism in the presence of initiators, either in solution^{1,4,8,9} or in

melt.^{2,3,5–7,10,11} MA has low reactivity toward free radicals due to its structural symmetry and deficiency of electron density around the double bond. However, it is an attractive reagent for modification of hydrophilicity of nonpolar polymers as it is difficult to homopolymerize, therefore normally only one monomer unit is grafted on each generated radical active site. In the case of polydienes such as NR, styrene–isoprene (SI), and styrene–butadiene–styrene (SBS) block copolymers, the grafting process can be done through two different mechanisms, i.e., radical-inducing grafting and thermal grafting via an ene mechanism.^{14–19} For the ene mechanism, high temperature (160–240°C) is required for the fixation of MA to polydiene backbone. In the case of the radical mechanism, the reaction usually occurs quickly and at a lower temperature than the ene reaction. Crosslinking has often taken place during free radical grafting reaction, which limits the high degree of grafting. It has also been reported that the grafting reaction of MA onto PE is frequently accompanied by a crosslinking reaction while the reaction with PP often induces a degradation reaction. As a result, the grafting efficiency of MA onto the PE, PP, or polymers containing PE or PP is poor. It has been reported that there are some monomers capable of acting as a donating electron to MA, leading to an enhancement of MA grafting efficiency onto polyolefins.^{2,7,20} One of these monomers is styrene (S), which has been found to effectively increase the grafting percentage of MA on PP and to decrease the PP degradation. It has been proposed that styrene reacts with MA to form a S-MA copolymer (SMA)

Correspondence to: P. Phinyocheep (scppo@mahidol.ac.th).

during the melt grafting process and that grafting of SMA leads to improvement in the grafting degree of MA on the polymer.^{2,7,20}

Currently, grafting of MA on NR has mostly been carried out in a solid phase by mixing the NR with MA in a kneader, a roll mill, or an internal mixer and a small percentage of MA grafting has been achieved and the crosslinking reaction was high.^{14,15,21} The MA-modified NR were used as compatibilizers in polyamide/NR blends^{14,15} and maleated NR/cassava starch blends.²¹ It is estimated in these two cases that the improvement of compatibility and mechanical properties of the blends are due to the intermolecular interaction between the MA polar groups grafted on NR and the amine end-group of polyamide or hydroxyl group of cassava starch molecules, respectively.

The study of determination and characterization of MA-modified polymers has been investigated in various publications. Some reports used the FTIR technique^{2,4–8,11,18,19,22,23} and some reports employed the titration method to determine the amount of MA grafted on the polymer backbone.^{1,6,9,10,14,20,22} It would be possible to widen the area of application of NR by chemical modification of NR with MA, as it is a way to introduce not only the polar moiety on the backbone of NR but also to introduce another type of reactive intermediate on the NR for further step modification if a required amount of the MA can be prepared and quantitatively determined. Therefore, in this study, the grafting of MA onto NR by a radical-induced grafting process using benzoyl peroxide (BPO) as a radical initiator was carried out. The NR was masticated to lower its molecular weight to avoid a premature crosslinking reaction prior to the grafting reaction. Various parameters affecting MA grafting efficiency, i.e., amount of BPO, MA, reaction temperature, and the presence of styrene as a comonomer were investigated. The use of the IR technique in combination with the titration method was explored to establish a calibration curve for determining the MA content grafted on the NR in the various conditions studied.

EXPERIMENTAL

Materials

Natural rubber (STR 5L) was supplied by Bangkok Rubber Company, Thailand. Maleic anhydride (97%) and tetramethylammonium hydroxide (TMAH, 25% in methanol) were used as received from Fluka. Benzoyl peroxide, a product from BDH Chemical Ltd., was used as received. Benzoic acid (98%), a product from Fluka, was sublimed before use.

TABLE I
Results of Viscosity Average Molecular Weight (M_v) of Natural Rubber at Different Mastication Times

Sample	Mastication time (min)	M_v
MNR0	0	1,200,000
MNR10	10	120,000
MNR15	15	93,000
MNR20	20	47,000

Mastication of natural rubber

Mastication of NR was carried out using a LAB TECH two-roll mill model LRM 150 to prepare rubbers having molecular weights lower than the original NR block rubber ($M_v = 1,200,000$ g/mol). Each batch of 300 g of block rubber was loaded onto the water-cooled mill. The nip gap was gradually reduced at the same time as the rubber was quartered. The mastication was continued for 5, 10, or 20 min at a temperature not exceeding 40°C before dumping the rubber from the mill.

The intrinsic viscosity, $[\eta]$ of the masticated natural rubber (MNR) was measured at 30°C, using an Ubbelohde viscometer. Toluene was used as a solvent. The viscosity average molecular weight (M_v) was calculated by the Mark–Houwink equation as shown in eq. (1).

$$[\eta] = KM_v^a \quad (1)$$

where for NR, $K = 3.31 \times 10^{-3}$ ml/g and $a = 0.71$ were used. The M_v values obtained are shown in Table I.

Grafting of maleic anhydride onto natural rubber

MNR was treated with 5–25% by mole of MA and 0.5–1.5% by mole of BPO without styrene or with 0.01 and 0.1% by mole of styrene in toluene solution (2.5–8% w/v). The experiment was performed in a round-bottom flask, equipped with a condenser and a magnetic stirrer under nitrogen atmosphere. The reaction was allowed to proceed at the specified temperature (60, 70, or 80°C). The mixture then was sampled at different reaction times and precipitated into excess methanol. The maleinized natural rubber (NR-g-MA) was obtained and purified by re-precipitation from chloroform into methanol. The resulting NR-g-MA was stored in chloroform solution.

Fourier transform infrared spectroscopy (FTIR)

The IR spectra of the rubber and the modified rubbers were recorded using a Perkin–Elmer System 2000 FTIR spectrometer. The dried rubber samples were dissolved in chloroform and cast as a thin film on a NaCl cell. The spectra of the grafted products were

recorded with 16 scans at a resolution of 4 cm^{-1} in the range of $4,000\text{--}500\text{ cm}^{-1}$.

Analysis of % MA grafting by the titration method

The amount of MA grafted onto the NR was determined by titration. NR-g-MA (1 g) dissolved in 100 ml chloroform was heated at 80°C with 2 ml of water for 10 h. The hydrolyzed product was precipitated in methanol. The resulting anhydride ring opened product was recovered and dried under vacuum. It was later dissolved in chloroform for hot titration with $2.2 \times 10^{-4}\text{ M}$ of TMAH in methanol. The TMAH was previously standardized with benzoic acid used as a primary standard. Two drops of 1% bromophenol blue was used as an indicator. When the coloration remained for 1 min, the end point was achieved. The MA content was determined from eq. (2):

% MA grafting (wt %) =

$$[(98 \times C_t \times V_t) / (2 \times C_p)] \times 100 \quad (2)$$

Where C_t and V_t are the concentration (mol/l) and volume (l) of the TMAH solution, respectively. C_p is the concentration of the rubber solution (wt %). The molecular weight of MA is 98 and the end point was achieved with 2 equivalent moles of acid group presented. This methodology was verified by the titration of MA and succinic anhydride with TMAH.

RESULTS AND DISCUSSION

Evidence of maleic anhydride grafting on natural rubber

The mechanism of a radical-induced MA grafting onto a polyolefin backbone has been well established.^{2,4,7} The reaction starts with hydrogen abstraction on the polymer backbone by radical species, generated from the decomposition of a radical-type initiator. The formed macroradical subsequently reacts with MA. In this study, BPO is used as a radical initiator for grafting MA on NR. The NR has a highly *cis*-1,4- polyisoprenic structure. It possesses labile allylic protons in every repeating unit. These protons are prone to hydrogen abstraction by radical active species generated from radical initiators such as AIBN and BPO similar to the grafting process of MA on SI and SBS block copolymers.^{18,19} The reaction mechanism of MA grafting on NR is therefore proposed in Figure 1. The BPO is decomposed into phenyl active radicals under heat. The radical generated then abstracts a proton on the NR backbone, preferably at an allylic position. The formed rubber radical will subsequently react with the MA, forming a macroradical of a succinic anhydride unit attached to the NR chain. Radical termination may then be achieved by radical chain transfer reac-

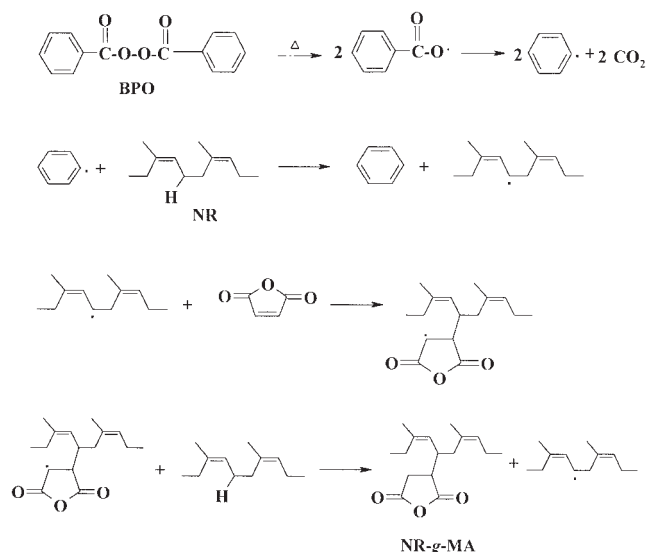


Figure 1 Proposed mechanism between maleic anhydride with natural rubber in the presence of benzoyl peroxide.

tion onto another rubber chain, resulting in a so-called maleic anhydride-grafted natural rubber (NR-g-MA). If the grafting process occurs, the MA fixed on the rubber chain will be in the form of a succinic anhydride ring. IR spectroscopy has been widely used for the identification of grafted anhydride residues. The characteristic signals of $\text{C}=\text{O}$ of a cyclic-five-membered ring of anhydride are normally observed in cm^{-1} as two peaks, i.e., unconjugated $\text{C}=\text{O}$ at $1,870\text{--}1,845$ (weaker) and $1,800\text{--}1,775$ (stronger) and conjugated $\text{C}=\text{O}$ at $1,860\text{--}1,850$ (weaker) and $1,780\text{--}1,760$ (stronger).²⁴ The elimination of unreacted MA from the grafting process is therefore important. The grafting of MA on MNR20 was performed by using 10% by mole of MA and 1% by mole of BPO in toluene solution. At the end of the reaction, the grafted rubber was precipitated in methanol and purified by reprecipitation in methanol. The ungrafted MA was then eliminated as the MA is soluble in methanol. The FTIR spectra in $4,000\text{--}500\text{ cm}^{-1}$ regions for starting NR and the NR-g-MA, using MNR20 are shown in Figures 2 (a and b), respectively. Figure 2(a) shows significant signals of $\text{C}=\text{C}$ of NR at $1,660$ and 835 cm^{-1} . Figure 2(b) indicates two extra absorption signals at $1,855$ and $1,778\text{ cm}^{-1}$, which can be assigned to asymmetric and symmetric $\text{C}=\text{O}$ stretching vibration modes of five-membered cyclic anhydride, respectively. This observation is similar to the grafting of MA on PE, PP, SI, and SBS based polymers.^{2-4,16,18,19} This evidence can therefore be used to confirm that the MA had grafted onto the NR backbone in a manner similar to several reports of the form of a succinic anhydride unit. However, spectrum b in Figure 2 also reveals an absorption signal around $1,720\text{ cm}^{-1}$, which can be attributed to a carbonyl group of carboxylic acid. The succinic anhy-

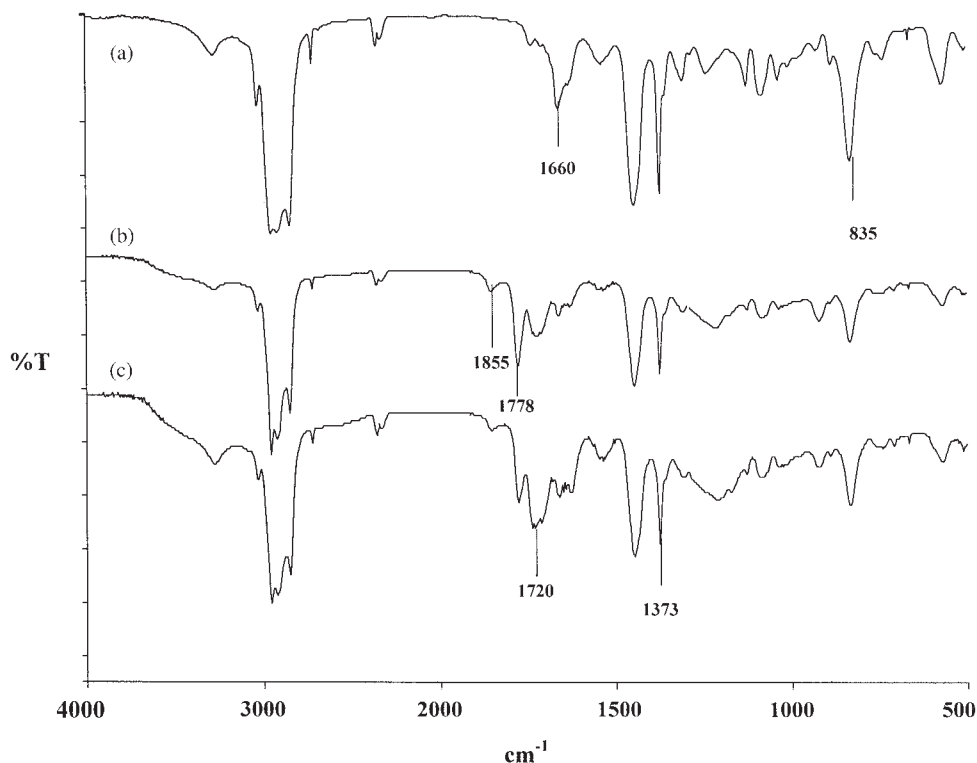


Figure 2 FTIR spectra of (a) natural rubber, (b) maleic anhydride grafted NR (NR-g-MA), and (c) hydrolyzed NR-g-MA.

dride unit attached to the NR was sensitive to moisture and a hydrogen donor molecule such as hydroxyl or amino functions. In the presence of a small amount of water, the anhydride ring can be opened, leading to the formation of carboxylic acid as shown in Figure 3. The reaction of MA-modified NR was carried out under nitrogen atmospheric pressure, however, the NR contains non rubber constituents such as fatty acid and proteins.²⁵ It is postulated that the succinic anhydride unit can be opened either during the grafting reaction by these non rubber constituents or during the purification process using methanol. Consequently, the signal of carboxylic acid is detected at $1,720\text{ cm}^{-1}$ in Figure 2(b).

When the NR-g-MA was heated at 80°C in the presence of water, the cyclic anhydride unit was hydrolyzed, resulting in the appearance of strong absorption peak around $1,720\text{ cm}^{-1}$, which can be assigned to the signal of C=O stretching of carboxylic acid function, as shown in Figure 2(c).

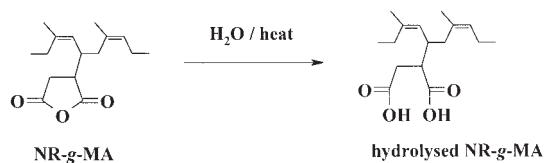


Figure 3 Hydrolysis reaction of maleic anhydride grafted natural rubber (NR-g-MA).

In some conditions of MA grafting onto NR, the gel formation was detected. This was not surprising as the grafting reaction that occurred through the radical mechanism (shown in Fig. 1); the formed rubber macroradical can interact with the macroradical of a succinic anhydride attached to the NR as shown in Figure 4(a) and the formed rubber macroradicals can interact with each other as shown in Figure 4(b), depending probably on the concentration of the radical species and the concentration of the reaction medium. The reaction between the acid groups, generated from an anhydride ring opening, can also react with the remaining anhydride moiety, causing the crosslinking reaction as shown in Figure 4(c).

It was found in our studies that, after the NR-g-MA obtained was dried and kept in solid form for a few days, incompletely redissolution was observed. It can be assumed that the partially hydrolyzed anhydride moiety mentioned earlier may progressively induce the reaction with another anhydride group present on the polymer backbone, as shown in Figure 4(c). Thus, it is not surprising that about 50% gel content was found in most of the cases.

The chemical structure of the NR-g-MA was also analyzed by $^1\text{H NMR}$. It was found that the characteristic signal of the proton attached to C=C of the polyisoprenic structure at 5.2 ppm was unchanged. A very weak signal of the proton of the succinic anhydride was detected at 2.3 ppm. This may be because

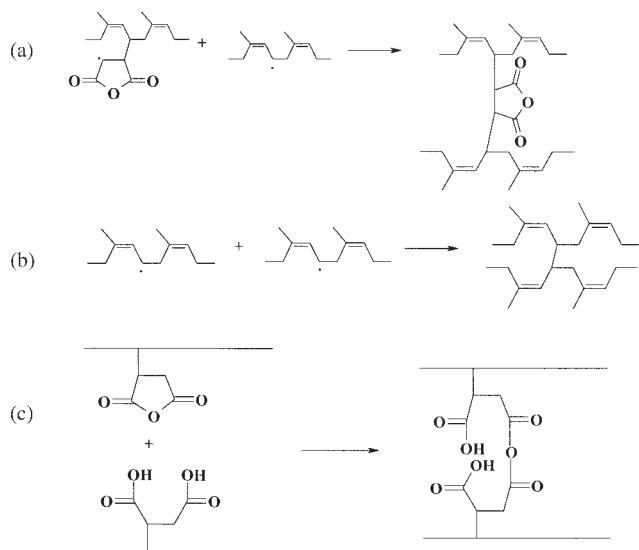


Figure 4 Proposed crosslinking reaction during the radical-induced maleic anhydride (MA) grafting onto natural rubber (NR).

little MA grafting was achieved. The signal of poly-(maleic anhydride) at 4.5 ppm was not observed.¹⁸

Determination of maleic anhydride grafting percentage

Sclavons *et al.*²² studied the determination of anhydride content of PP-g-MA by FTIR and titration. They eliminated the free ungrafted MA by heating and washing the modified PP. The titration was performed with the hydrolysis of the succinic anhydride into the

acid group. Mehrabzadeh *et al.*¹¹ studied the MA-modified EPDM and they used the absorption signals in the IR spectrum to detect the amount of MA grafting in relation to the results obtained from potentiometric titration of the hydrolyzed form of EPDM-g-MA. Cha and White⁶ studied the grafting of MA on PP. They established a calibration curve from the intensity of the carbonyl absorption peak area at 1,785 cm^{-1} divided by the intensity of the signal at 1,165 cm^{-1} characteristic of the methyl group of PP (A_{1785}/A_{1165}), and the results of MA content were obtained from a nonaqueous titration.

In this work, the percentage by weight of MA grafting onto NR at various reaction conditions was determined by titration of hydrolyzed NR-g-MA with TMAH after elimination of free and ungrafted MA by precipitation in methanol, and then refluxing with water. The intensity of the carbonyl absorption peak area of carbonyl function at 1,855, 1,778, or 1,720 cm^{-1} before hydrolysis divided by that of the methyl (CH_3) of the rubber chain at 1,373 cm^{-1} for different reaction conditions was compared with the % MA obtained from the titration. The plots of % MA obtained from the titration against the $A_{1778} + A_{1720}/A_{1373}$ gave a straight line with a slope of 0.7211 and an R^2 equal to 0.9917 as shown in Figure 5. A calibration curve in Figure 5 was therefore established and used for further analysis of NR-g-MA products. The MA grafting percentages in other reaction conditions were then calculated from the ratio of $A_{1778} + A_{1720}/A_{1373}$ in the IR spectrum as in the following eq. (3):

$$\% \text{ MA grafting} = 0.7211 \times (A_{1778} + A_{1720}/A_{1373}) \quad (3)$$

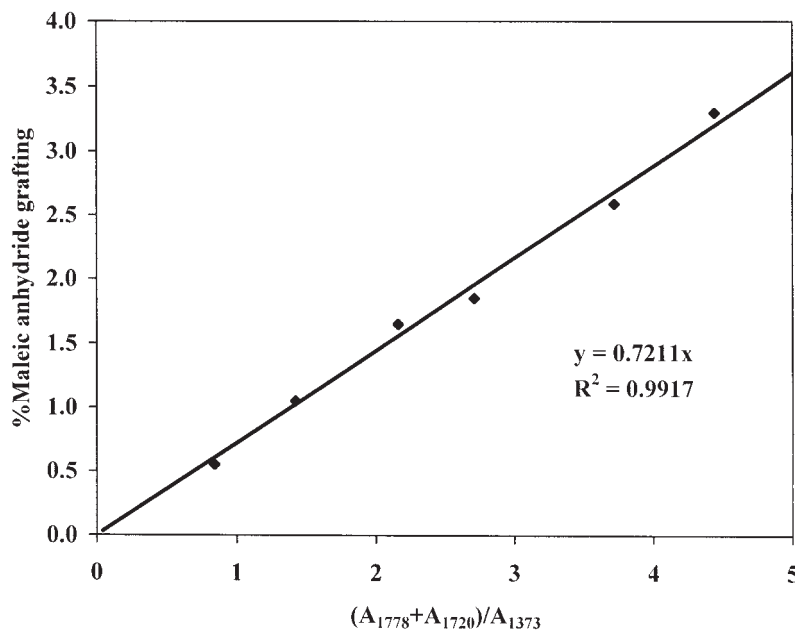


Figure 5 FTIR calibration curve for quantitative measurement of % maleic anhydride grafting onto NR.

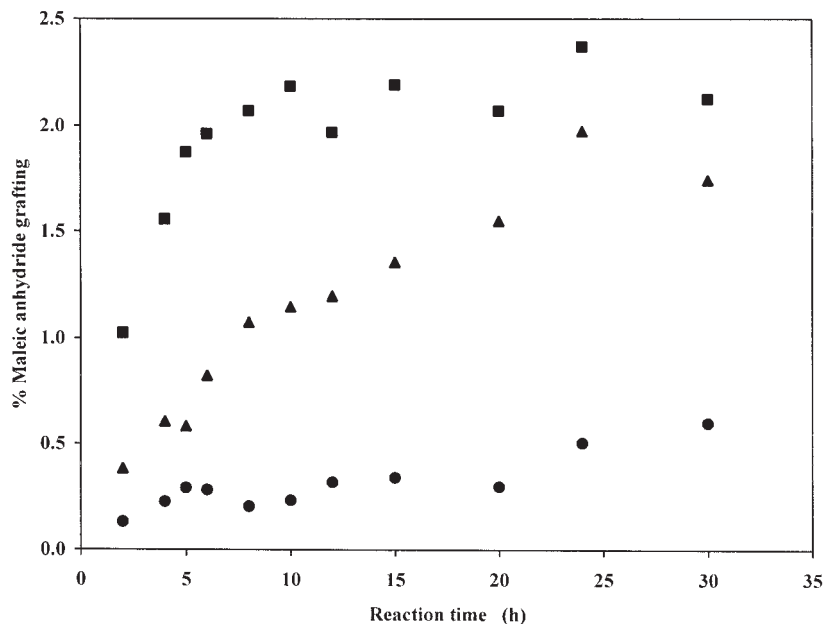


Figure 6 Effect of reaction time and temperature on % maleic anhydride grafting onto NR using 5% rubber, 1.0% BPO, and 10% MA at (●) 60°C, (▲) 70°C, and (■) 80°C.

Parameters affecting the maleic anhydride grafting efficiency

Effect of reaction time and temperature

To study the effect of reaction time and temperature, MNR20 ($M_v = 47000$) was also used. The reaction of MA with MNR20 was carried out in the presence of 10% MA, 1.0% BPO in 5% toluene solution at 60, 70, and 80°C. The % MA grafted on the rubber was determined from eq. (3). Figure 6 shows the plots of % MA found against various reaction times at three different reaction temperatures. It can be seen that the amount of incorporated MA increased at longer reaction times. This trend was observed for all reaction temperatures. However, at a reaction temperature of 70°C, the conversion went through a maximum, when approximately 1.8% MA is introduced at 24 h, and then decreased. The fixation of MA on the rubber backbone at 80°C is faster than at 60 and 70°C. By using the reaction at 80°C, the degree of MA grafting progressively increased at the early state of the reaction (5 h), and then a slight increase of grafting yield was performed at longer reaction time. Figure 6 also indicates that the increase of the reaction temperature results in an increase of the degree of MA grafting. The best result was obtained at the reaction temperature of 80°C. This suggests that, at higher reaction temperatures, the dissociation of BPO is faster, leading to an acceleration of the radical formation on the rubber backbone and subsequently the collision between the radical species formed and the MA. Thus the rate of grafting was increased. The maximum percentage of MA grafting was about 2.2%, which indicated that

only 15% yield was obtained. This may be because the radical generated on the rubber chain is located at the allylic position, which can be delocalized for stabilization, resulting in the difficulty of reaction between the delocalized macroradical and the unreactive MA molecule.

Effect of initiator concentration

The influence of BPO content (0.5–1.5% by mole) on the grafting degree of MA on the rubber was investigated by using 5% rubber (MNR20) treated with MA (10% by mole) at 80°C. Figure 7 shows results of % MA found at various reaction times for the grafting reaction using various amounts of BPO. This figure reveals that, by increasing the amount of initiator from 0.5 to 1.0% by mole, the grafting content increased about two times. This may be explained by the fact that, by increasing the amount of BPO, the concentration of the radical sites on the rubber chain may be increased, leading to an increase of the possibility of the reaction between MA and the rubber chain, which is similar to the results obtained for grafting of MA onto polyolefins.^{4,10} However, when the amount of BPO was increased to 1.25 and 1.5% by mole, the % MA grafting increased at the early stage of reaction (2 h of reaction time), thereafter % MA could not be determined, as the crosslinking reaction occurred in both cases. This is because an increase of the BPO leads to an increase in the amount of active radical sites, thus the chance of intermolecular reaction or crosslinking reaction as shown in Figure 4 increases. Gel content determina-

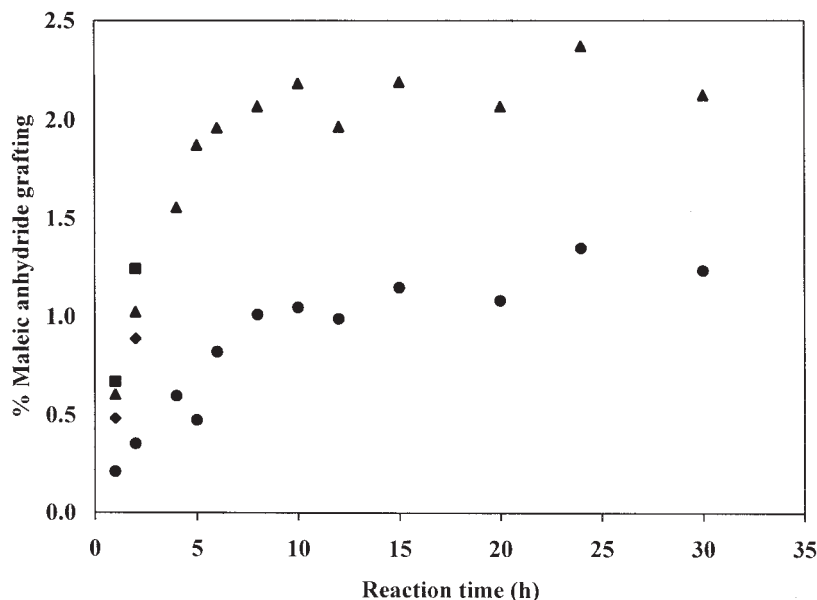


Figure 7 Effect of initiator concentrations on % maleic anhydride grafting onto NR using 5% rubber, 10% MA at 80°C with various amounts of benzoyl peroxide (BPO): (●) 0.5% BPO, (▲) 1.0% BPO, (◆) 1.25% BPO, and (■) 1.5% BPO.

tion revealed also that the insoluble fraction of functionalized rubber increased with increasing the peroxide concentration. These results are similar to the MA-modified PP and EPDM reported in the literature.^{7,11}

Effect of amount of maleic anhydride

The efficiency of grafting is likely to be dependent on the role of MA diffusion into the NR phase. As has

already been found, only about 15% yield of MA was fixed on the rubber backbone when 10% by mole of MA was used. Various amounts of MA (5, 10, 20, and 25% by mole) were investigated for the reaction with MNR20 in the presence of 1% by mole of BPO at 80°C. The plots of % MA grafting against various reaction times at different amounts of MA used are shown in Figure 8. It can be seen that the incorporation of MA on the rubber chain at a constant initiator (BPO) in-

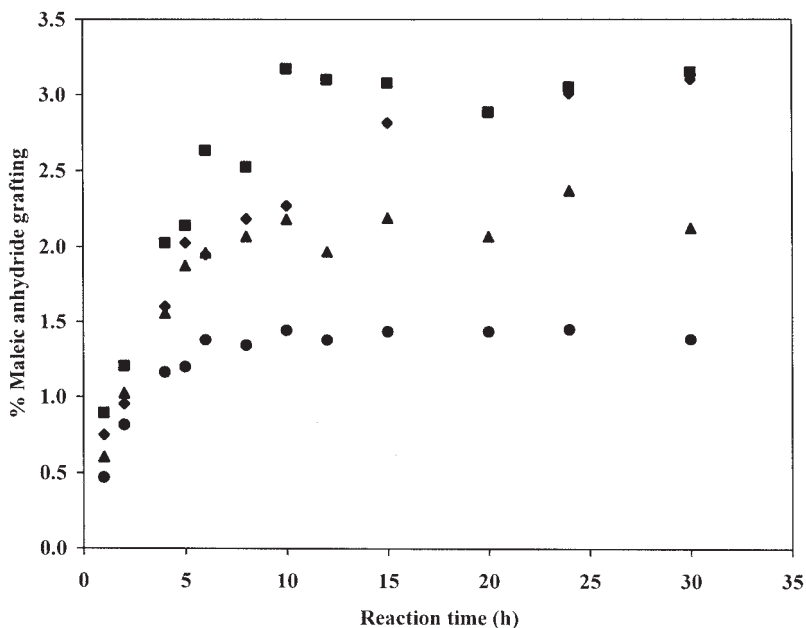


Figure 8 Effect of maleic anhydride concentrations on % maleic anhydride grafting onto NR using 5% rubber, 1.0% BPO at 80°C: (●) 5% MA, (▲) 10% MA, (◆) 20% MA, and (■) 25% MA.

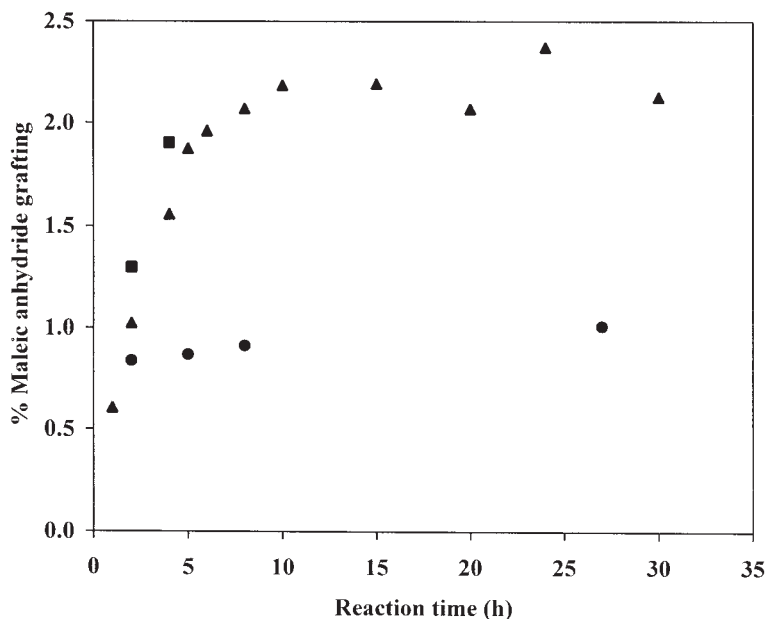


Figure 9 Effect of rubber concentrations on % maleic anhydride grafting onto NR using 10% MA, 1.0% BPO, and 80°C: (●) 2.5% rubber, (▲) 5% rubber, and (■) 8% rubber.

creased significantly with an increase in the amount of MA from 5 to 10% by mole. The MA diffusion into NR is likely to be increased with an increase of MA concentration. Further increase of MA concentration (20 or 25% by mole) gave slightly higher percent grafting but the maximum percent grafting was found at about 3% by mole, which means only 12% yield of MA is fixed on the rubber chain. Thus, there was no improvement of MA content when a high concentration of MA was added. This result is similar to the grafting of MA onto EPDM.¹¹ Generally, it is considered that the radical species in the system induce the excitation of MA. At a fixed concentration of peroxide, the increase of MA concentration decreases the concentration of excited MA as the excited MA is quenched by the MA ground state, therefore less excited MA is grafted onto NR.

Effect of rubber concentration

Figure 9 shows the influence of rubber (MNR20) concentration on the grafting degree of using 10% by mole of MA and 1% BPO at 80°C. It can be seen that the grafting degree increases with an increase in the rubber concentration from 2.5 to 5%. When increasing the rubber concentration to 8%, only a slight increase of the grafting degree was observed at up to 4 h reaction times, thereafter the grafting degree could not be determined as gel formation was observed in the reaction medium. This suggests that increasing the rubber concentration too much allows the rubber chains to become closer; this may facilitate the intermolecular reaction between the generated macroradical as

shown in Figure 4, thus leading to gel formation rather than grafting of MA on the rubber chain.

Effect of molecular weight of masticated natural rubber

Figure 10 shows the effect of different molecular weights of the masticated NR used as the starting materials for the grafting reaction of MA. The condition involved the use of 5% rubber concentration, 10% by mole of MA, and 1% by mole of BPO at 80°C. It can be seen that the grafting degree increased with the decrease of the molecular weight of natural rubber. The % MA grafting of MNR20 was higher than that of MNR10, which was higher than the use of MNR5. This may be due to the higher mobility of the rubber chain, which is achieved when the molecular weight of the NR is lower, and this leads to a better reaction between the macroradical and the MA. Therefore, a higher degree of MA grafting can be achieved for a lower molecular weight NR.

Effect of styrene on grafting percentage

It was mentioned in the case of MA modified polyolefins that the MA has low reactivity with itself and its grafting onto the polymer backbone is due to the deficiency of electron density around the double bond as well as the high steric hindrance resulting from disubstitution.¹⁻⁴ It was also found in our case that the grafting efficiency of MA on the NR was poor. Styrene monomer has been reported in the literature to be used as an electron donor to activate the MA mono-

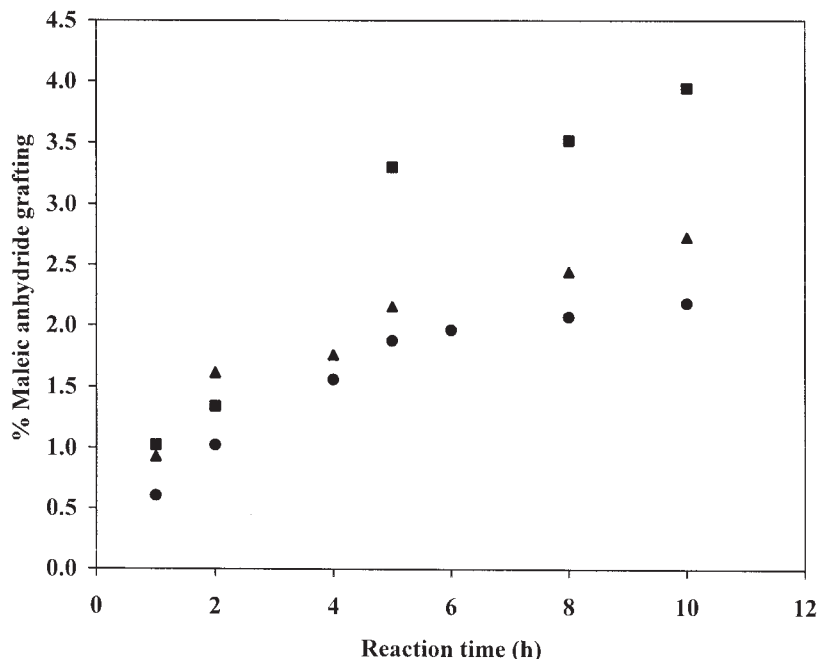


Figure 10 Effect of styrene concentrations on % maleic anhydride grafting onto NR using 5% rubber, 10% MA, 1% BPO, and 80°C: (●) 0% styrene, (▲) 0.01% styrene, and (■) 0.1% styrene.

mer for grafting polymerization on PE and PP.^{2,7,20} Styrene has a higher ability to polymerize than MA, therefore it not only can graft directly onto a PP chain or onto a MA graft but can also graft onto another S molecule. The styrene comonomer may serve as a medium to bridge the gap between the NR macroradical and the MA. In the case of styrene-assisted MA grafting onto PP, increasing the amount of S resulted in increasing the amount of MA as well as S grafted on the polymer backbone.⁷ It is our objective to have mainly MA grafted onto NR to enhance the polarity of NR as well as to introduce a reactive function on NR backbone. Therefore, to minimize the long sequence of S grafted on NR as well as SMA copolymer, a small amount of S was planned to be used as an activator for MA grafting. Figure 10 shows the results of % MA grafting on MNR20 using 1% by mole of BPO, without S, with 0.01 and 0.1% by mole of S. It was found that a very small amount of S (0.01% by mole) affected an increase of % MA grafting at an early stage of reaction time (up to 2 h) but at longer reaction times there is not much difference in % MA with or without the S. The explanation is that at early stage of reaction time, when S is added, S and MA can interact with each other one-to-one to form a charge transfer complex (CTC), which increases electrical asymmetry of the double bond of MA, resulting in enhancing the MA's reactivity, hence increasing the % MA grafting. The S can easily react with the macroradical as well as copolymerize with the MA; the S might react first with the rubber chain, and then subsequently react with the MA, leading to an increase in the amount of MA

incorporated into the rubber molecule. When the S was consumed, the free MA could still be grafted on the NR macroradical. In the case of 0.1% S, it was not surprising to find that the % MA of the resulting rubber was significantly higher than in the presence of 0.01% MA or without the presence of S at a longer reaction time. At a higher amount of S, the formation of CTC is higher, hence higher % MA grafting was obtained.

FTIR spectra of NR-g-MA and NR-g-(MA-S) are shown in Figure 11. In the case of NR-g-(MA-S), the intensity of the carbonyl absorption band at 1,778 cm^{-1} of NR-g-(MA-S) compared to the signal of CH_3 at 1,373 cm^{-1} is much stronger than that of NR-g-MA. A new absorption band at 704 cm^{-1} was observed and it could be assigned to the characteristic absorption of the grafted styrene. As the small amount of S (0.1 and 0.01% by mole) was used, all of the S might form the CTC complex with MA, the homopolymerization of S might not occur, and the signal characteristic of the polystyrene at 758 cm^{-1} was not observed, nor the fingerprint at 2,000–1,600 cm^{-1} .

The influence of S on grafting degree of MA for three different molecular weights, i.e., MNR5, MNR10, and MNR20 was investigated by using 1% BPO and 10% MA at 10 h. The results shown in Figure 12 indicate that the % MA grafting increased up to two times when 0.1% by mole of S was used for all three types of MNR. The styrene is an effective comonomer for enhancing the grafting percentage of MA on NR even at relatively high molecular weight. This may be

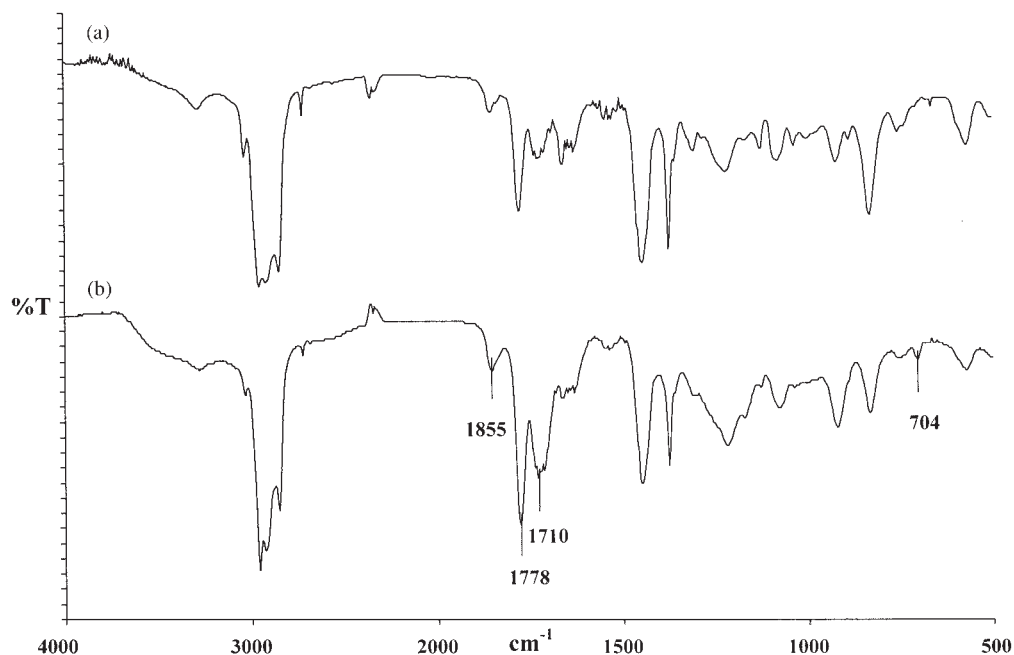


Figure 11 FTIR spectra of maleic anhydride grafted natural rubber (a) without the addition of styrene (NR-g-MA) and (b) with the presence of styrene [NR-g-(MA-S)].

due to the fact that the S can act as a good electron donating monomer to the MA through CTC.

CONCLUSION

Maleic anhydride can be grafted onto natural rubber by using a free radical process. The reaction time, temperature, initiator, rubber, and MA concentration

as well as the molecular weight of NR influence the grafting percentage of MA on the rubber backbone. The addition of styrene as a comonomer to the grafting system of MA onto NR significantly improved the grafting percentage of MA. It is proposed that the styrene plays a role as a charge transfer complex with MA. The styrene can react first with the rubber macroradical generated from the reaction of BPO initiator,

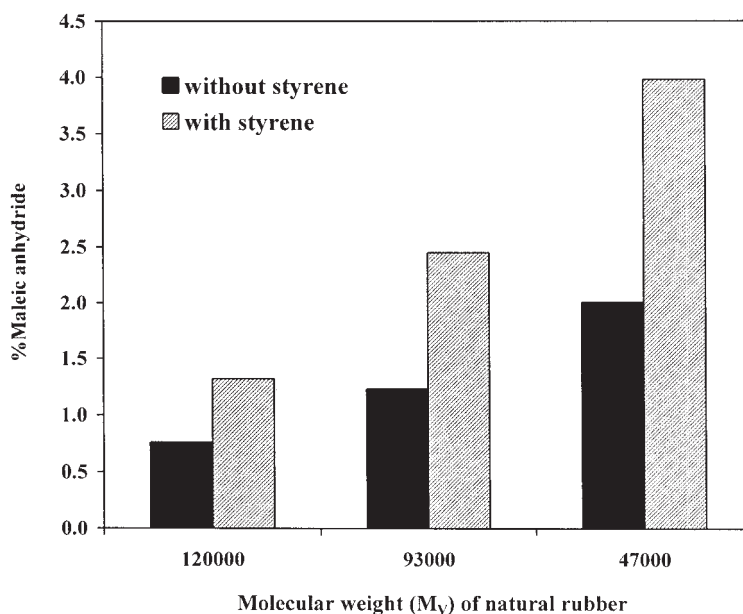


Figure 12 Effect of styrene and molecular weight of natural rubber on % maleic anhydride grafting onto NR using 5% rubber, 10% MA, 1% BPO, and 0.1% styrene at 80°C during 10 h.

followed by the reaction with MA molecules, leading to improvement of the grafting efficiency of MA.

The authors thank the Thailand Toray Science Foundation for financial support of this work. The scholarship from the Institutional Strengthening Program, Faculty of Science, Mahidol University, Thailand to J. Saelao is also appreciated.

References

- Priola, A.; Bongiovanni, R.; Gozzelino, G. *Eur Polym J* 1994, 30, 1047
- Samay, G.; Nagy, T.; White, J. L. *J Appl Polym Sci* 1995, 56, 1423
- Deng, J-P.; Yang, W-T.; Ranby, B. *Eur Polym J* 2002, 38, 1449
- Lu, B.; Chung, T. C. *J Polym Sci Part A: Polym Chem* 2000, 38, 1337
- Bettini, S. H. P.; Agnelli, J. A. M. *J Appl Polym Sci* 1999, 74, 256
- Cha, J.; White, J. L. *Polym Eng Sci* 2001, 41, 1227
- Li, Y.; Xie, X.; Guo, B. *Polymer* 2001, 42, 3419
- Machado, A. V.; Covas, J. A.; Duin, M. *Polymer* 2001, 42, 3649
- Li, H.; Chen, H.; Shen, Z.; Lin, S. *Polymer* 2002, 43, 5455
- Gaylord, N. G.; Mehta, M.; Mehta, R. *J Appl Polym Sci* 1987, 33, 2549
- Mehrabzadeh, M.; Kasaei, S.; Khosravi, M. *J Appl Polym Sci* 1998, 70, 1
- Cimmino, S.; Coppola, F.; D'Orazio, L.; Greco, R.; Maglio, G.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Ragosta, G. *Polymer* 1986, 27, 1874
- Kayano, Y.; Keskkula, H.; Paul, D. R. *Polymer* 1998, 39, 2835
- Axtell, F. H.; Phinyocheep, P.; Kriengchieocharn, P. *J Sci Soc Thailand* 1996, 22, 201
- Carone Jr, E.; Kopcak, U.; Goncalves, M. C.; Nunes, S. P. *Polymer* 2000, 41, 5929
- Derouet, D.; Phinyocheep, P.; Boccaccio, G.; Brosse, J. C. *J Nat Rubb Res* 1991, 6, 39
- Brosse, J. C.; Campistron, I.; Derouet, D.; El Hamdaoui, A.; Houdayer, S.; Reyx, D.; Ritoit-Gillier, S. *J Appl Polym Sci* 2000, 78, 1461
- Mitov, Z.; Velichkova, R. *Eur Polym J* 1993, 29, 597
- Aimin, Z.; Chao, L. *Eur Polym J* 2003, 39, 1291
- Jia, D.; Luo, Y.; Li, Y.; Lu, H.; Fu, W.; Cheung, W. L. *J Appl Polym Sci* 2000, 78, 2482
- Nakason, C.; Kaesman, A.; Homsin, S.; Kiatkamjornwong, S. *J Appl Polym Sci* 2001, 81, 2803
- Sclavons, M.; Carlier, V.; De Roover, B.; Franquinet, P.; Devaux, J.; Legras, R. *J Appl Polym Sci* 1996, 62, 1205
- Garcia-Martinez, J. M.; Laguna, O.; Areso, S.; Collar, E. P. *J Appl Polym Sci* 1999, 73, 2837
- Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: UK, 1991
- Nor, H. M.; Ebdon, J. R. *Prog Polym Sci* 1998, 23, 143