Synthesis of NR-g-PMMA by "Grafting from" Method Using ATRP Process

Lapporn Vayachuta,[1] Pranee Phinyocheep,[1,2] Daniel Derouet,[3] Sagrario Pascual[3]

[1]Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Payathai, Bangkok 10400, Thailand
[2]Institute of Molecular Biosciences, Mahidol University, Salaya Campus, Puthamonthon, Nakornpathom 73170, Thailand
[3]UCO2M, LCOM-Chimie des Polymères, UMR CNRS 6011, Université du Maine, Avenue O. Messiaen, 72085 Le Mans Cedex 9, France

ABSTRACT: Grafting poly(methyl methacrylate) or PMMA from natural rubber (NR) using ATRP process, NR has to be transformed into bromoalkyl-functionalized NR (NRBr) acting as ATRP macroinitiator. The NRBr was prepared by two-step chemical modification i.e., epoxidation and epoxide ring opening reaction using a nucleophile containing bromine atom such as 2-bromopropionic acid (**A1**) and 2-bromo-2-methylpropionic acid (**A2**). The fixation of **A1** and **A2** on 4-methyl-4-octene, a model representing one repeat unit of NR, modified by epoxidation was prior studied and it was found that the resulting addition products from **A2** using as ATRP initiator for MMA gave a better control of $\overline{M}_{n,\exp}$ and low PDI of PMMA than that from **A1**. Then, the NR was transformed into ATRP rubber macroinitiator via epoxidation, followed by epoxide ring addition with only **A2**. ^{1}H NMR was employed to determine the amount of **A2** addition units on NR, which is considered to be the same amount of grafting sites for ATRP of MMA. The grafting of PMMA was then successfully carried out from the NR backbone by ATRP process. The PMMA grafts of the NR-g-PMMA were indeed linked to the NR backbone via ester linkage of the **A2** unit. The PMMA grafts could be cleaved from the NR backbone by acid hydrolysis, while PMMA grafting by other conventional radical reaction could not be done. Then, the average MW of PMMA grafts after separation using acetone extraction was evaluated. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 508–520, 2011

Key words: atom transfer radical polymerization (ATRP); chemical modification; ^{1}H NMR; natural rubber; poly(methyl methacrylate)
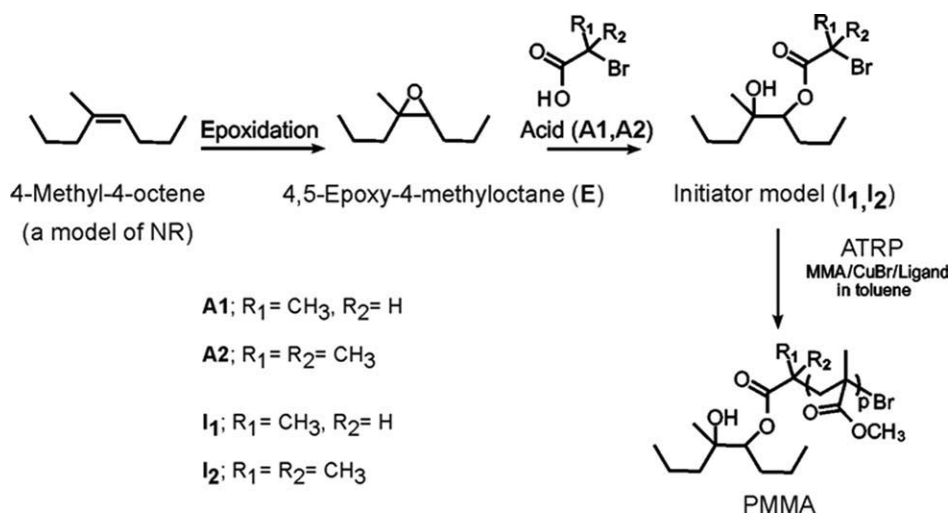
INTRODUCTION

Natural rubber (NR), a cis-1,4-polyisoprenic biomaterial collected from Hevea brasiliensis, is known for many special properties, including high resilience, good "green" strength, and remarkable elastic behavior. Nowadays, there is an increasing issue concerning environmental awareness, therefore NR becomes more attractive for scientists because it is a renewable resource. It has been used in various sectors in particular for tires, rubber seals, and gloves. Graft copolymerization of methyl methacrylate (MMA) onto NR has been considerably investigated to incorporate the plastic character of poly(methyl methacrylate) (PMMA) into the elastomeric character of NR[1–7] to diversify its area of applications. In general, grafting of PMMA onto NR chains was performed using "grafting from" method, performed in organic or water media using a conventional radical polymerization in the presence of radical initiators such as benzoyl peroxide (BPO) and redox systems.[1–6] However, such strategy can not provide predetermined graft sites of PMMA and it did not give the possibility to well determine the molecular graft size. In addition, it often produces high amount of PMMA homopolymer as well as partially crosslinked product.

Nowadays, controlled/living radical polymerizations (CRP),[8] have been introduced and they are considered to be methods that can control the lifetime of active radical species, hence reduce the radical transfer reaction as well as coupling reaction. Among the reported CRP methods, atom transfer radical polymerization (ATRP)[9,10] is recommended for graft copolymerization purpose as the initiation of the polymerization should be effective only from initiating sites that are prior created on the polymer main chains, hence the formation of homopolymer

Scheme 1 Strategy to functionalize 4-methyl-4-octene into ATRP initiators and the use to prepare PMMA by ATRP.

should be avoided. To monitor the grafting reaction by this method, halogen atom has to be introduced on the polymer backbone. In the case of NR, fixation of halogen atom on the NR molecular chain to transform the NR into ATRP macroinitiators can be carried out by two methods; via one-step modification or two-step modification. The first pathway includes the reactions of halogenation and hydrohalogenation.[11] However, these methods are often accompanied by side reactions such as cyclization. It was reported that the synthesis of (ethylene–propylene–diene terpolymer)-*graft*-PMMA (EPDM-*g*-PMMA) through ATRP, bromination of EPDM could be performed using *N*-bromosuccinimide/azobisisobutyronitrile system.[12] The resulting brominated EPDM was used as a macroinitiator to initiate the ATRP of MMA. However, the PMMA molecular graft size was not investigated. Two-step modification reaction to introduce halogen atom on the polymer backbone was reported by Coiai et al. for graft copolymerization of styrene and (meth)acrylic monomers on ground tire rubber (GTR) particles by ATRP.[13] The bromine atom was introduced via oxidation then nucleophilic reaction with 2-bromoisobutyrylbromide (BIBB). In this case, determination of the active sites for ATRP required complicated system. In our laboratory, two-step functionalization of NR into photosensitive rubber has been well practiced via epoxidation followed by epoxide ring addition with photosensitive acid.[14] The epoxide ring opening reaction with other types of nucleophiles such as alcohol derivatives was also successfully carried out and reported.[15] If the nucleophilic reagent bearing halogen atom was used to react with the epoxide ring on the NR molecular chain, the modified form of NR will be acted as macroinitiator for ATRP system. It will be then able to use

for "grafting from" of various vinyl monomers under ATRP concept. As NR is derived from natural resource and it contains non-rubber constituents which may effect on chemical modifications and also structure elucidation of the NR macroinitiators, our work is therefore first of all concerning the study on model of NR using 4-methyl-4-octene which is the simplest model of one repeat unit of NR (*cis*-1,4-polyisoprene) before going further to the study on NR.

In this work, 4-methyl-4-octene was epoxidized using *m*-chloroperbenzoic acid in organic solution, then nucleophilic addition at oxirane ring with two types of bromoalkyl carboxylic acids i.e., 2-bromopropionic acid (**A1**) and 2-bromo-2-methylpropionic acid (**A2**) were investigated (Scheme 1). The resulting brominated model compounds (**I₁** and **I₂**) were explored as ATRP initiators for polymerization of MMA which was carried out in the presence of two types of ligand i.e., *N*-(*n*-octadecyl)-2-pyridylmethanimine (NODPMI, -$C_{18}H_{37}$) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) ligands[16–18] (Scheme 2). The results obtained were further applied to transform NR into NR macroinitiator for ATRP by two-step modification i.e., epoxidation followed by ring opening reaction with the selected acid. The amount of ATRP initiator units was considered to be the same amount of bromoalkyl carboxylic acid added on the modified NR,
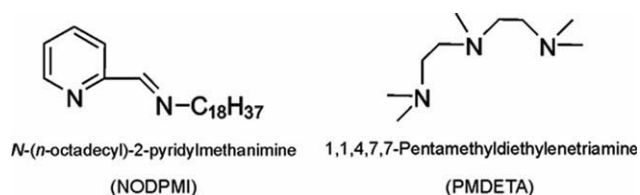
Scheme 2 Chemical structures of the amine ligands used.

which were determined using ^{1}H NMR before ATRP polymerization of MMA was carried out. The number-averaged molecular weight ($\overline{M}_n$) and polydispersity index (PDI) of PMMA grafts were determined by size exclusion chromatography (SEC) after separation of PMMA from the NR main chain by hydrolysis using trifluoroacetic acid, followed by acetone extraction.

EXPERIMENTAL

Materials

The 4-methyl-4-octene used as a model compound of NR (*cis*-1,4-polyisoprene) unit and its epoxidized derivative (4,5-epoxy-4-methyloctane, **E**) were synthesized according to the reported procedure.[15] Methyl methacrylate (MMA) (Acros Organics, 99%) was purified by washing three times with 10 wt % NaOH solution to remove an inhibitor, and then with distilled water. The washed MMA was dried on anhydrous $MgSO_4$ before distillation at 50°C under low pressure. Natural rubber latex (dry rubber content (drc) = 60%) was supplied by Bangkok Rubber Company, Thailand. Formic acid (98–100%, analytical grade) purchased from Merck and hydrogen peroxide (H_2O_2, 34 wt % standard grade) purchased from Ajax Chemicals, were used as received. Teric 16A16 (polyoxyethylene cetyl-stearyl ether with 16 polyoxyethylene units; Hydrophilic Lipophilic Balance: HLB = 15.2) from East Asiatic Company (Thailand) was used as received. Copper (I) bromide (99.99+ %) and aluminum oxide, activated neutral, were purchased from Aldrich and used as received. N-(n-octadecyl)-2-pyridylmethanimine (NODPMI, -$C_{18}H_{37}$) was synthesized according to the procedure reported by Haddleton et al.[16] 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99+ %), 2-bromopropionic acid (99+ %), 2-bromo-2-methylpropionic acid (98%), and trifluoroacetic acid (TFA) (≥98.0% were supplied by Acros Organics and used as received.

Characterization techniques

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 Fourier transform spectrometer. Samples were analyzed in solution of chloroform-D (99.8% purity; Spectrométrie Spin and Techniques) with tetramethylsilane (TMS) as the internal standard.

FTIR spectra were made with a Perkin–Elmer 1750 Fourier transform spectrophotometer in the 700–4000 cm^{-1}. Samples were analyzed in the form of thin films on NaCl disk.

Number-averaged molecular weights ($\overline{M}_n$) and polydispersity indexes (PDI) were measured using size exclusion chromatography (SEC) equipped with a Spectra SYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm^2) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 300 × 7.5 mm^2), and a Spectra SYSTEM RI-150 detector. THF was used as an eluent at a flow rate of 1 mL min^{-1}. Polystyrene standards (580–483 × 10^3 g mol^{-1}) were used to calibrate the SEC.

Addition of 2-bromoalkyl carboxylic acid on 4,5-epoxy-4-methyloctane

The 4,5-epoxy-4-methyloctane, **E,** Scheme 1 (1 g, 7.03 mmol) was dissolved in toluene (1.7 wt %). The 2-bromopropionic acid (**A1**) (6.45 g, 0.042 mol) or 2-bromo-2-methylpropionic acid (**A2**) (7.04 g, 0.042 mol) was then added to the solution. The reaction mixture was stirred during 6 h at 90°C for **A1** and 110°C for **A2**. When the reaction was completed, saturated $NaHCO_3$ was added to eliminate the excess acid. The organic phase was washed three times with distilled water, and then dried on anhydrous $MgSO_4$ overnight. After filtration, toluene was eliminated under vacuum. The crude mixture was fractionated by liquid chromatography using an open column chromatography, filled with silica and dichloromethane was used as an eluent. The chemical structures of the resulting products (I_1 and I_2) were analyzed by ^{1}H NMR and FTIR spectroscopy.

Typical procedure for ATRP of MMA using I_1 and CuBr/ N-(n-octadecyl)-2-pyridylmethanimine (NODPMI)

Cu(I)Br (0.058 g, 0.40 mmol) and NODPMI (0.28 g, 0.80 mmol) were placed into a Schlenk tube. The tube was fitted with a rubber septum and then flushed with dry nitrogen and vacuum three times to remove oxygen. MMA (4.65 g, 0.046 mol), I_1 (0.26g, 0.40 mmol), and toluene (50 wt % with respect to MMA) were placed in another Schlenk tube, and the oxygen was removed by freeze-pump-thaw cycles. The mixture was transferred via a cannula, to the Schlenk tube containing CuBr and NODPMI (Scheme 1). The reaction mixture was degassed by three freeze-pump-thaw cycles and back-filled with nitrogen. Afterwards, the mixture was placed into an oil bath thermostated at 90°C. Samples were taken at various reaction times using a degassed syringe to follow monomer conversion by ^{1}H NMR spectroscopy, as well as number-averaged molecular weights and polydispersity indexes by size exclusion chromatography (SEC). The catalyst was removed from the samples by passing the polymer solution through a chromatography column filled with alumina. The

polymer was then precipitated in methanol, filtered, and dried under vacuum at room temperature until constant weight.

The progress of MMA polymerization was followed by ^{1}H NMR spectroscopy and the MMA conversions were determined from ^{1}H NMR spectra of crude mixtures using eq. (1).

$$\text{MMA conversion (\%)} = \frac{I_{3.57}}{(I_{3.57} + I_{3.70})} \times 100 \quad (1)$$

where, $I_{3.57}$ is the area of $-OCH_3$ signal of PMMA and $I_{3.70}$ is the area of $-OCH_3$ signal of residual MMA.

Synthesis of epoxidized natural rubber (ENR)

NR was partially epoxidized in latex medium using procedure reported in the literature.[19] NR latex (30% dry rubber content) was stabilized using Teric 16A16 (3 phr) at room temperature for 12 h in a reactor. Then, 20 mol % formic acid and 40 mol % of H_2O_2 were slowly added to the stabilized latex. After 24 h of stirring at 50°C, the resulting ENR latex was precipitated in methanol and the obtained ENR was dried under vacuum until constant weight. The level of epoxidation was determined from ^{1}H NMR spectrum by ratio of integrated area of the signal at 2.72 ppm ($I_{2.72}$) corresponding to the proton on oxirane rings of the epoxidized units to that at 5.13 ppm ($I_{5.13}$) characteristic of proton on carbon–carbon double bonds of NR units as shown in eq. (2).[19] The degree of epoxidized NR units contained in the synthesized ENR was found equal to 17.8 % (**ENR-17.8**).

$$\text{Epoxidized NR units (\%)} = \frac{I_{2.72}}{I_{2.72} + I_{5.13}} \times 100 \quad (2)$$

Synthesis of NR macroinitiator (NRBr) by addition of A2 on ENR

About 5 g of **ENR-17.8** were dissolved in toluene (5 wt/v% of ENR in toluene). Then, 12.5 g of **A2** (75 mmol, [acid]/[ENR units] molar ratio = 6) were added to the solution and the reaction mixture was placed into an oil bath thermostated at 110°C during 6 h. At the end of the reaction, the mixture was precipitated in methanol. The NR macroinitiator (NRBr) obtained was purified by re-dissolving in toluene and precipitating in methanol. This purification process was performed several times until remaining acid was totally eliminated. The purified NRBr was then dried under vacuum at room temperature until constant weight. Resulting polymer was analyzed by FTIR, ^{1}H and ^{13}C NMR. The composition of the synthesized NRBr was determined from its ^{1}H NMR spectrum, using the following eqs. (3–5).

Bromoalkyl-functionalized NR units (o%)

$$= \frac{I_{4.90}}{(I_{4.90} + I_{4.05} + I_{2.72})} \times E\% \quad (3)$$

Residual epoxidized units (m%)

$$= \frac{I_{2.72}}{(I_{4.90} + I_{4.05} + I_{2.72})} \times E\% \quad (4)$$

Allyl alcohol units (p%) $= \frac{I_{4.05}}{(I_{4.90} + I_{4.05} + I_{2.72})} \times E\% \quad (5)$

where, $I_{4.90}$, $I_{4.05}$, and $I_{2.72}$ are the integrations of proton signals of bromoalkyl functionalized NR units, allyl alcohol units, and residual epoxidized units, respectively, and $E\%$ is the percentage of starting ENR units. The degree of bromoalkyl-functionalized NR units contained in the rubber was found equal to 5.1 % (**NRBr-5.1**).

Typical procedure for synthesis of NR-*g*-PMMA by ATRP

About 0.021 g (0.15 mmol) of Cu(I)Br and 0.107 g (0.30 mmol) of NODPMI were introduced into a Schlenk tube sealed with a rubber septum. The Schlenk tube was then deoxygenated with three vacuum/nitrogen-filled cycles. A solution of 3.7 mL (33 mmol) of MMA and 0.25 g (0.15 mmol of bromoalkyl-functionalized NR units) of **NRBr-5.1** in 35.7 mL of toluene was introduced into another Schlenk tube and the oxygen was removed by freeze-pump-thaw cycles. The solution mixture was transferred via a cannula to the Schlenk tube containing CuBr and NODPMI. The reaction mixture was deoxygenated by three freeze-pump-thaw cycles and back-filled with nitrogen. Afterwards, the mixture was placed into an oil bath thermostated at 90°C. Samples were withdrawn from reaction mixture at various reaction times, using a deoxygenated syringe for conversion monitoring by SEC analysis. Each sample was dissolved in CH_2Cl_2 and passed through an alumina column to remove the catalyst. The copolymer was precipitated in methanol, filtered, and dried under vacuum at room temperature until constant weight.

Hydrolysis of NR-*g*-PMMA

Twenty milligrams of NR graft copolymer was dissolved in 2 mL of dichloromethane. Then, 2 μL of trifluoroacetic acid (TFA) was added and the mixture was stirred at room temperature.[20] After 24 h, the solvent was removed under vacuum and acetone was added to dissolve PMMA grafts. The solution was filtered to eliminate NR backbone and then, PMMA grafts were precipitated in hexane. The product was filtered and dried under vacuum at room temperature until constant weight. After
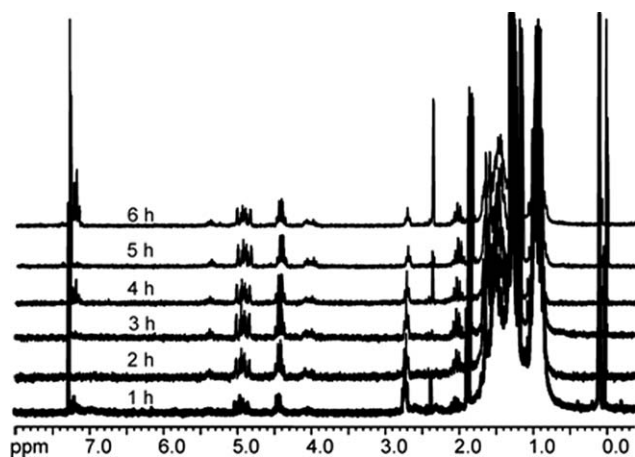
Figure 1 ^{1}H NMR spectra of crude mixture of reaction of **A1** upon **E** at various reaction times ([**A1**]/[**E**] = 6 mol mol^{-1} at 90°C for 6 h using 1.7 wt % of **E** in toluene).

purification, ^{1}H NMR spectroscopy was used to confirm that PMMA was separated without remaining NR. The number-average molecular weight ($\overline{M}_{n,\text{SEC}}$) and polydispersity index (PDI) of PMMA grafts were then measured by SEC. While the residual rubber part dissolved in hexane was further analyzed by ^{1}H NMR spectroscopy after precipitation in methanol and dried under vacuum.

RESULTS AND DISCUSSION

Two-step modification of 4-methyl-4-octene, a model of NR

Before investigation on the synthesis of NR-g-PMMA, functionalization of 4-methyl-4-octene selected as a model compound of NR (cis-1,4-polyisoprene), into ATRP initiator by a two-step procedure was considered to obtain bromoalkyl-functionalized compounds. It consists at first to epoxidize 4-methyl-4-octene, and then to add a bromoalkyl carboxylic acid on the oxirane ring formed (Scheme 1). The epoxidation was performed using m-chloroperbenzoic acid that acts as an oxidizing agent to generate 4,5-epoxy-4-methyloctane (**E**). For the addition step, two acids were chosen to react with oxirane rings: 2-bromopropionic acid (**A1**) and 2-bromo-2-methylpropionic acid (**A2**), resulting in formation of bromoalkyl functionalized models acted as ATRP initiators, **I₁** and **I₂** respectively. Two aspects were considered: the ability of **A1** and **A2** to react with oxirane ring and the ability of **I1** and **I2** to initiate an ATRP polymerization of MMA.

^{1}H NMR analysis (Fig. 1) of the crude mixtures obtained from the reaction of **A1** on **E** taken at various reaction times and cleared out of the residual acid (**A1**) showed a decrease of the signal characteristic of the oxirane ring protons at 2.63 ppm, and

increasing of intensities at 4.39 and 4.88 ppm corresponding to proton signals of the addition products. The crude mixture obtained after 6 h was cleaned out of the residual acid, was fractionated by liquid chromatography using an open column filled with silica and dichloromethane as an eluent, to isolate each component contained in the mixture. The product isolated in each fraction was analyzed by ^{1}H NMR spectroscopy. It was noted that the crude mixture was composed of several products and the main component of O-(2-hydroxy-2-methyl-1-(n-propyl)pentyl)-2-bromopropionate (**I₁**, 46.3%) was found. Figure 2 clearly shows two characteristic proton signals of the addition product (**I₁**) at 4.39 ppm and 4.88 ppm which are assigned to —CH(OC(O)CH(CH₃)Br)— and —CH(OC(O)CH-(CH₃)Br)— protons, respectively. Other signals of methyl and methylene protons were found in ppm at 0.84 (CH₃—CH₂—), 1.11 (—C(OH)(CH₃)—), 1.14-1.73 (—CH₂—), and 1.78 (—OC(O)CH(CH₃)Br). On the FTIR spectrum of **I₁** (Fig. 3), two strong absorption bands were noted at 1736 and 3505 cm^{-1} corresponding to C=O stretching vibration of ester group and to OH stretching vibration of hydroxyl, respectively. Two allyl alcohol side products coming from rearrangements of the starting epoxide (**E**) in acid medium (Scheme 3): (2-(n-propyl)hex-1-en-3-ol (**B₁**, external allyl alcohol) and 5-methyloct-5-en-4-ol (**B₂**, internal allyl alcohol) were found, which could be noted from the signals in ^{1}H NMR of —C(=CH₂)—) at 4.93 ppm (2H) and —CH₂—HC=C— at 5.28 ppm (1H), respectively.

Similar to the study with **A1**, the reaction between **A2** and **E** was carried out. The mixture was withdrawn periodically, analyzed by ^{1}H NMR spectroscopy after clearing out of the remaining **A2**, to follow the progress of the reaction. A decrease of the signal at 2.63 ppm corresponding to the characteristic of the oxirane ring protons was observed,
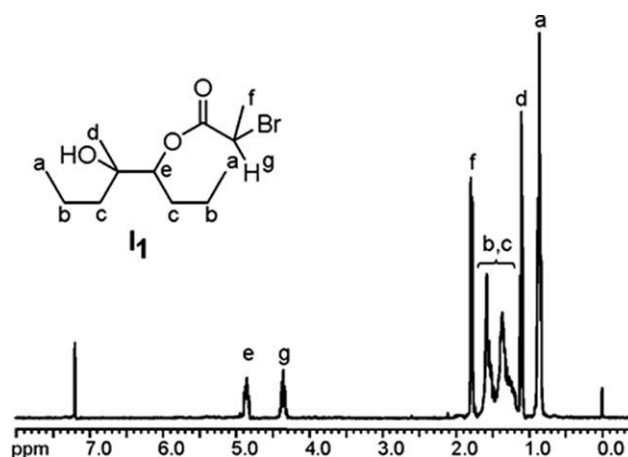

Figure 2 ^{1}H NMR spectrum of O-(2-hydroxy-2-methyl-1-(n-propyl)pentyl)-2-bromopropionate (**I₁**).
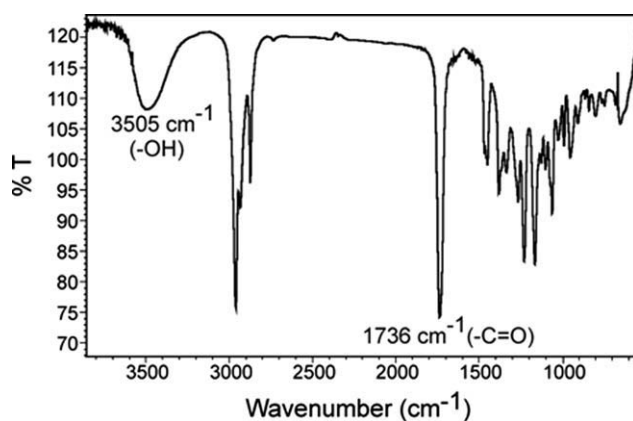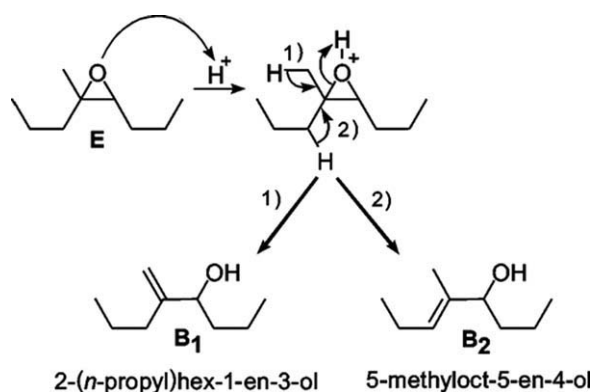
Figure 3 FTIR spectrum of *O*-(2-hydroxy-2-methyl-1-(*n*-propyl)pentyl)-2-bromopropionate (**I₁**).

Figure 4 ¹H NMR spectrum of *O*-(2-hydroxy-2-methyl-1-(*n*-propyl)pentyl)-2-bromoisobutyrate (**I₂**).

together with the increasing intensities of the signals of the addition product at 1.89 and 4.89 ppm. After fractionation of the resulting mixture by liquid chromatography, ¹H NMR spectroscopy (Fig. 4) of the main product (I₂, 44.4%) shows the signals at 1.89 and 4.89 ppm, assigned to —CH(OC(O)C(CH₃)₂Br)— and —CH(OC(O)C(CH₃)₂Br)— protons, respectively. Other signals of methyl and methylene protons were found in ppm at 0.85 (CH₃—CH₂—), 1.12 (—C(CH₃)(OH)—), and 1.15–1.67 (—CH₂—). On the other hand, it was also confirmed by the analysis using FTIR spectroscopy that two strong absorption bands of the addition product (I₂) at 1735 and 3421 cm⁻¹, characteristic of C=O stretching vibration of ester group and of OH stretching vibration of hydroxyl, respectively, were observed (similar to I₁). Two allyl alcohols (**B1** and **B2**) were also found as side products in this reaction.

The results from ¹H NMR and FTIR reveal that two-step modification of 4-methyl-4-octene into ATRP initiators (**I₁** and **I₂**) was successful. These data are useful for further utilization of two-step modification to transform NR into ATRP macroinitiator.

ATRP of MMA initiated by bromoalkyl functionalized models

The bromoalkyl addition products **I₁** and **I₂** (Scheme 1) were two functionalized models acting as initiators for polymerization of methyl methacrylate (MMA) via an ATRP process. Two different ligands i.e., *N*-(*n*-octadecyl)-2-pyridylmethanimine (NODPMI) and 1,1,4,7,7-pentamethyldiethylene triamine (PMDETA) were used to study the ATRP of MMA with the two initiators prepared. A kinetic study, the dependence of the number-averaged molecular weight ($\overline{M}_n$) and polydispersity indexes (PDI) with MMA conversion were considered. This part aimed to find out a suitable bromoalkyl initiator and ligand that perform a good control and well-defined PMMA.

In the first study, ATRP of MMA initiated from the synthesized model **I₁** and **I₂**, were carried out in toluene at 90°C using CuBr/NODPMI as a catalytic system. Samples were taken off the reaction mixture at various reaction times to follow MMA conversion
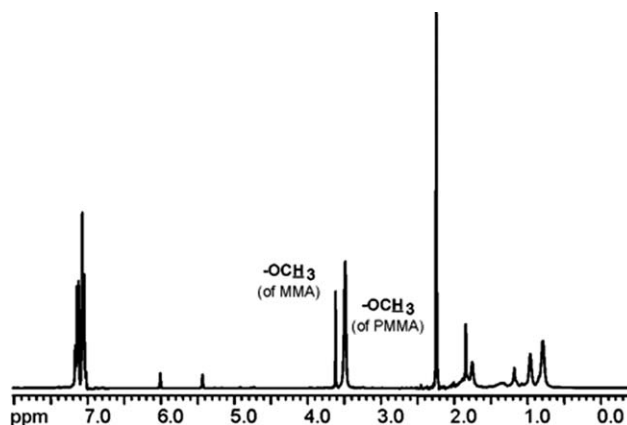

Scheme 3 Rearrangement of 4,5-epoxy-4-methyloctene (**E**) in acid medium.

Figure 5 Typical ¹H NMR spectrum of PMMA containing residual MMA during ATRP of MMA from I₁.
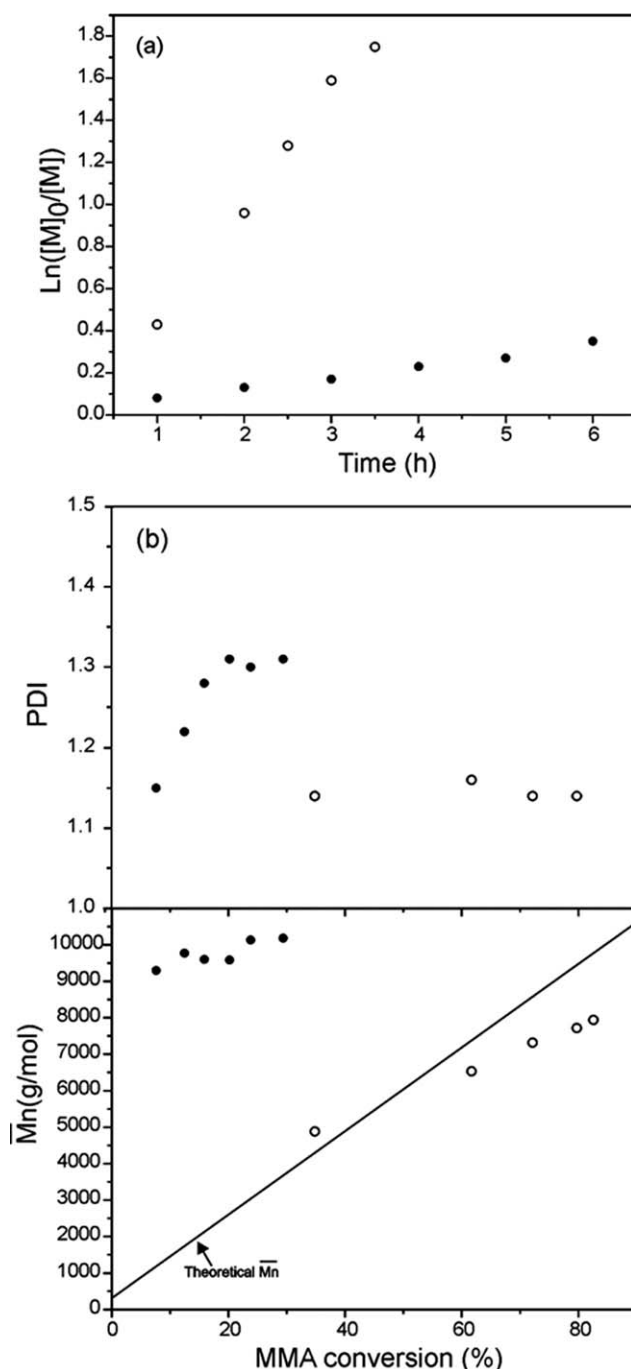
Figure 6 Kinetic study of ATRP of MMA initiated by $I_1(\bullet)$ and $I_2(\bigcirc)$ using CuBr/NODPMI at 90°C in toluene 50 wt % ($[MMA]_0/[I_1 or I_2]_0/[CuBr]_0/[NOPMI]_0 = 115/1/1/2$). (a) Kinetic plots and (b) progress of $\overline{M}_n$ and PDI with MMA conversion.

by ^{1}H-NMR spectroscopy. Figure 5 shows typical ^{1}H NMR spectrum of PMMA obtained from initiator model I_1, showing the signal of $-OCH_3$ at 3.57 and 3.70 ppm corresponding to methoxyl protons of PMMA and residual MMA, respectively. The MMA conversion (%) was determined using eq. (1) shown in Experimental. Plots of $\ln([M]_0/[M])$ versus time was then carried out to follow the kinetic of ATRP

reaction using initiators I_1 and I_2. Figure 6(a) shows the linearity of the $\ln([M]_0/[M])$ versus time for both initiators. This implies the constant concentration of the growing radicals.[8,9] Figure 6(b) shows the relationship of $\overline{M}_n$ and PDI obtained from SEC analysis, with MMA conversion. The straight line represents the theoretical number-number average molecular weight calculated. The initiator I_2 provided an increase of experimental number-averaged molecular weight ($\overline{M}_{n,exp}$) of PMMAs with conversion and the obtained PDIs remained below 1.2. The $\overline{M}_{n,exp}$ of PMMA initiated from I_1 was higher than the calculated ones and PDIs increased with MMA conversion but were still below 1.4 [Fig. 6(b)]. It seems likely that I_2 led to a better control of $\overline{M}_{n,exp}$ and PDI than I_1.

The same initiators were also used for the ATRP of MMA using CuBr/PMDETA as a catalytic system in similar reaction conditions. The linearity of $\ln([M]_0/[M])$ versus time was found with both initiators. Similar trend of the polymerization rate can be seen in Figure 7(a). The experimental number-averaged molecular weight ($\overline{M}_{n,exp}$) of PMMA initiated from I_2 increase linearly with MMA conversion and PDIs were $\sim$ 1.3 [Fig. 7(b)]. The $\overline{M}_{n,exp}$ of PMMA initiated from I_1 were higher than the calculated ones and they increased at higher MMA conversion. The initiator I_1 provided the PDIs between 1.4 and 1.5. With the same MMA conversion using CuBr/PMDETA as a catalyst, the ability to control $\overline{M}_{n,exp}$ was also shown to be better with I_2 than with I_1. These results showed that initiator I_2 is more efficient than the initiator I_1 to provide well-defined PMMAs. This may be due to the stabilization effect of the radical formed after releasing bromine atom during the early stage of the ATRP. Indeed, initial species obtained from the initiator I_2 are tertiary radicals, which are more stable than secondary ones coming from the initiator I_1.[21] The initiator which led to better stabilized species after the dissociation of halogen atom to generate radicals, resulted in PMMAs with lower PDIs.[22] The less stabilization of the radical formed from initiator I_1 may also result in early termination, hence less amount of initiator I_1 is active for further polymerization. Therefore, the $\overline{M}_{n,exp}$ of PMMA initiated from I_1 was higher than the calculated ones.

The effects of two structures of bidentate and tridentate ligands i.e., N-(n-octadecyl)-2-pyridyl-methanimine (NODPMI) and 1,1,4,7,7-pentamethyl-diethylenetriamine (PMDETA), respectively, on ATRP of MMA were studied in toluene medium. Using the same initiator (I_2), it was found that the chemical structure of the ligand dramatically affected the apparent polymerization rate (Fig. 8). PMDETA gave higher polymerization rate than NODPMI [Fig. 8(a)]. This result is in accordance
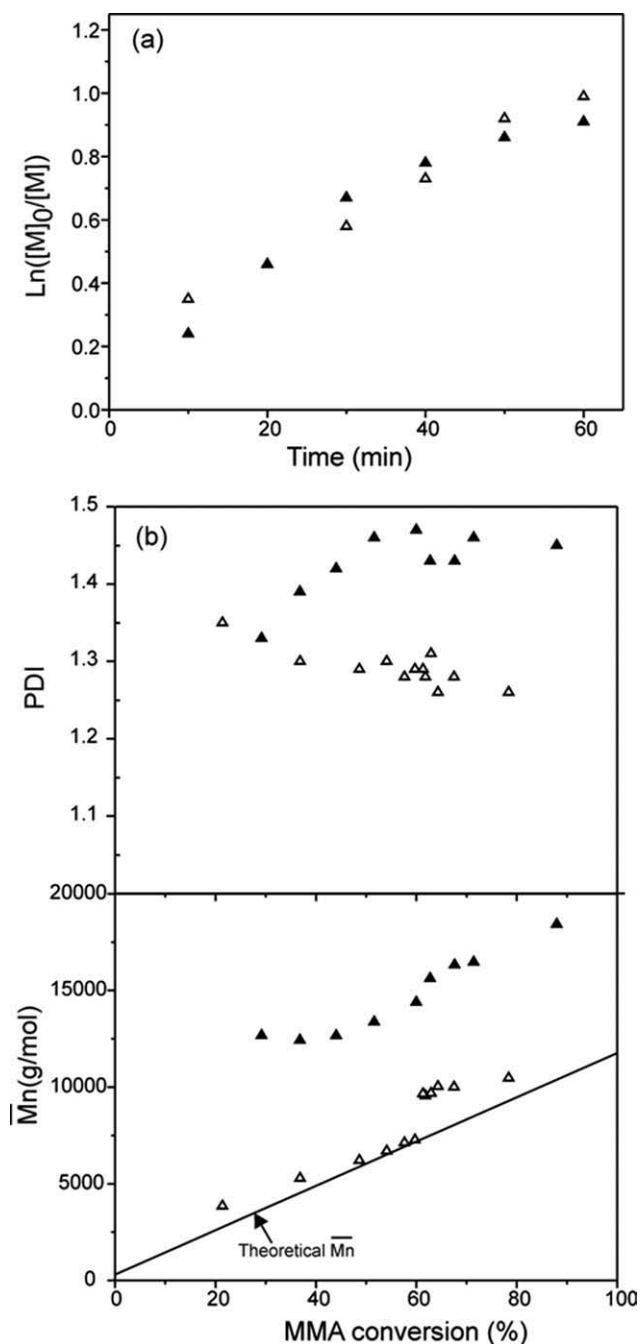
be noted that polydispersity index of PMMA obtained from the system using NODPMI ligand was less than 1.2 which is narrower than in the case of the system using CuBr/PMDETA. This can be explained from the fact that the faster the release of halogen atom, the higher concentration of free radicals is present, hence greater the possibility of recombination termination or transfer reaction is
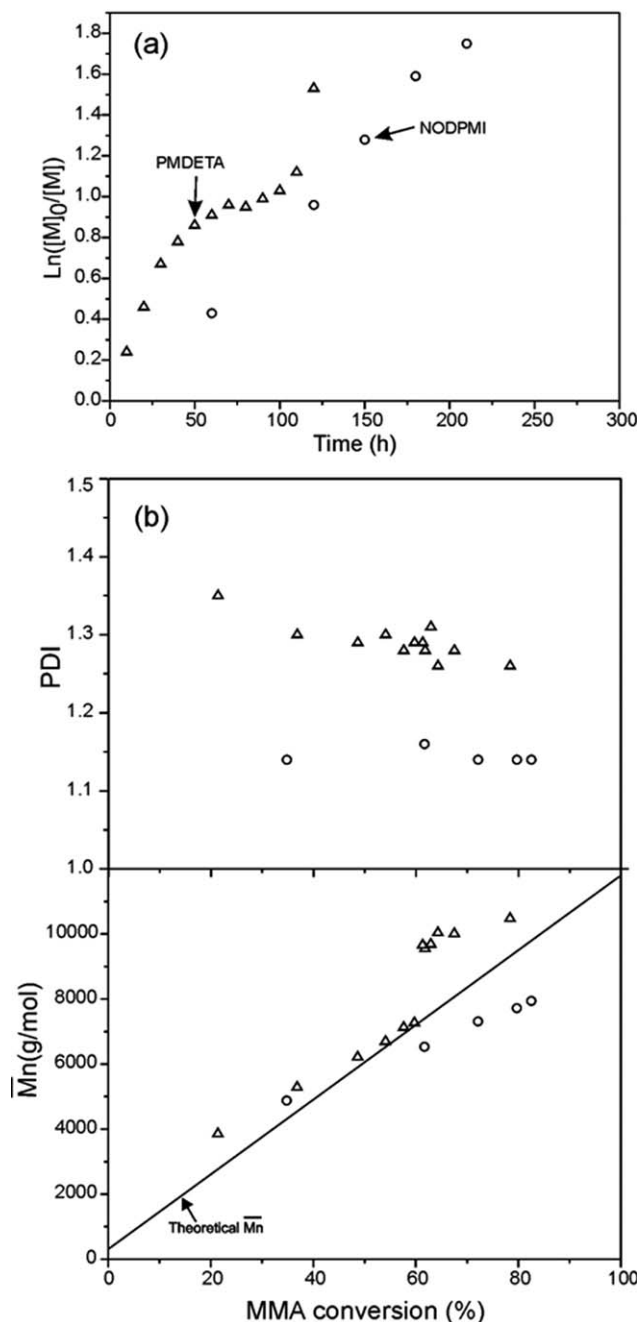

Figure 7 Kinetic study of ATRP of MMA initiated by I_1(▲) and I_2(Δ) using CuBr/PMDETA at 90°C in toluene 50 wt % ($[MMA]_0/[I_1 or I_2]_0/[CuBr]_0/[PMDETA]_0 = 115/1/1/1$). (a) Kinetic plots and (b) progress of $\overline{M}_n$ and PDI with MMA conversion.

with the work reported that the general order of activation rate constant of Cu complex for amine ligand is tetradentate > tridentate > bidentate.[18,23] The use of PMDETA complex with CuBr resulted in higher MMA conversion than in the case of using NODPMI ligand. As a result, the faster polymerization rate in the ATRP using PMEDTA as a ligand has an effect on PDIs of the resulting PMMA. It can

Figure 8 Kinetic study of ATRP of MMA initiated by I_2 using NODPMI(○) and PMDETA(Δ) at 90°C in toluene 50 wt % ($[MMA]_0/[I_2]_0/[CuBr]_0/[NOPMI]_0 = 115/1/1/2$ or $[MMA]_0/[I_2]_0/[CuBr]_0/[PMDETA]_0 = 115/1/1/1$). (a) Kinetic plots and (b) progress of $\overline{M}_n$ and PDI with MMA conversion.
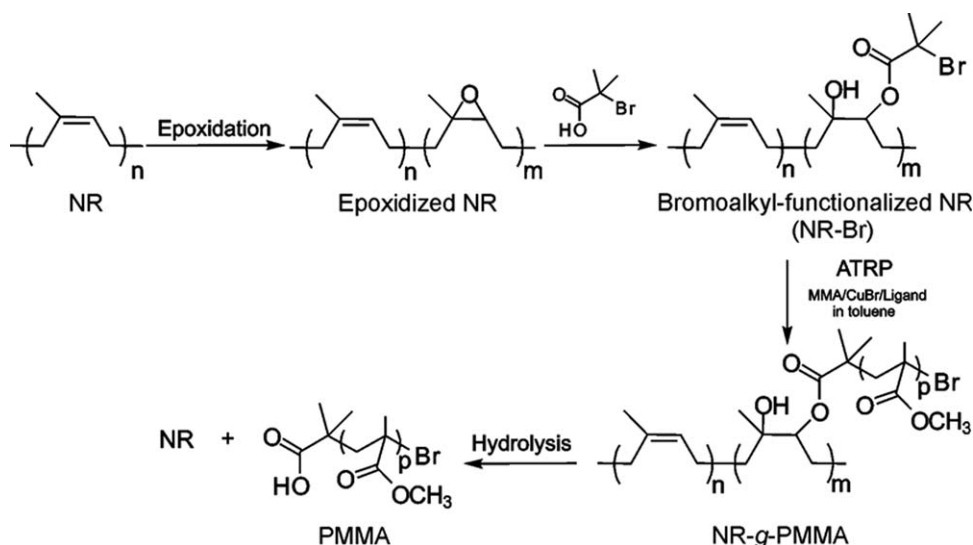
Scheme 4 Strategy to prepare NR-*g*-PMMA using "grafting from" technique from bromoalkyl functionalized NR using ATRP concept and cleavage of PMMA grafts from NR backbone by hydrolysis.

taken place in the system. Therefore, higher PDIs were found in the system using CuBr/PMDETA than the system using CuBr/NODPMI.

Two-step modification of NR for preparation of bromoalkyl-functionalized NR (NRBr)

To prepare NR-*g*-PMMA by "grafting from" technique using ATRP concept, the NR has to be transformed into bromoalkyl-functionalized NR (NRBr) which will act as ATRP macroinitiator. The NR transformation was done using two-step modification (Scheme 4) in which the first step involved the epoxidation of NR carried out in latex stage using performic acid generated *in situ* from hydrogen peroxide and formic acid.[19] This is considered as the most economical process for preparation of epoxidized NR (ENR) as the reaction was carried

out in water at the original state of NR obtained from *Hevea* tree. The formation of oxirane rings along NR chains was confirmed by both FTIR and ^{1}H NMR spectroscopies as shown in Figures 9 and 10, respectively.[14,19] FTIR spectrum of ENR showed a new absorption band at 870 cm^{-1} corresponding to
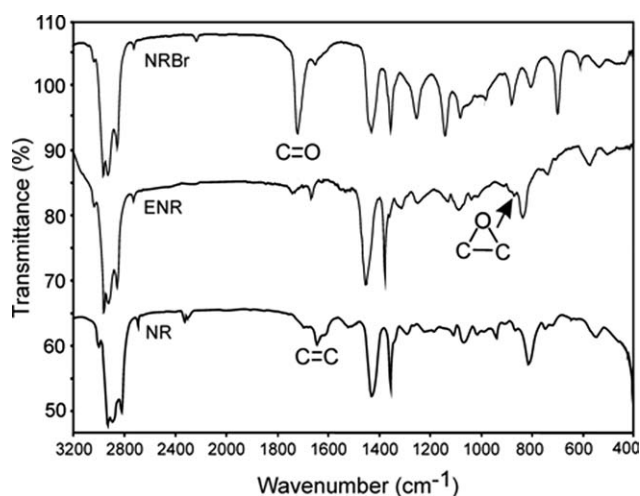

Figure 10 ^{1}H NMR spectra of NR, ENR-17.8, and NRBr-5.1 and NR-*g*-PMMA.

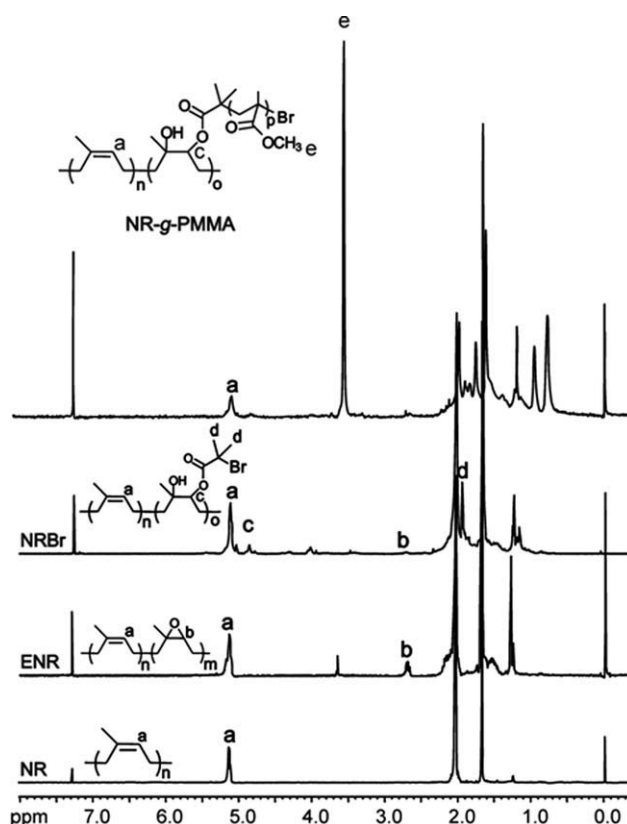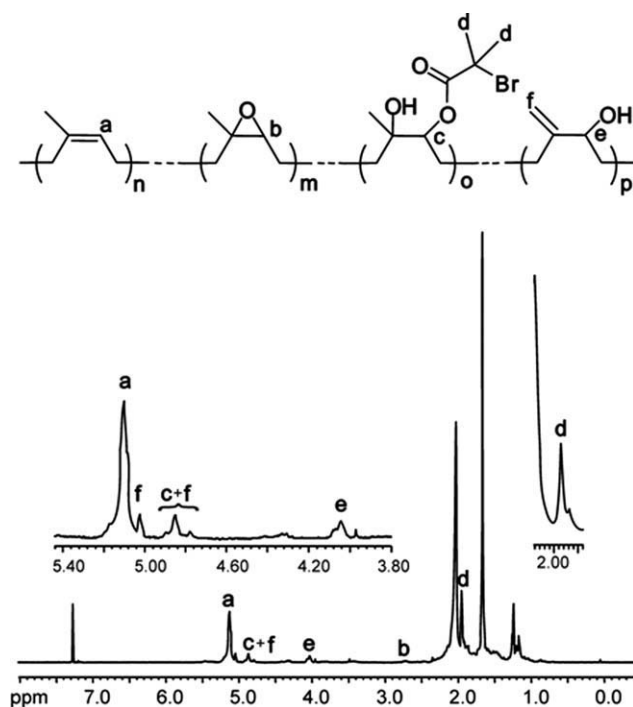**Figure 9** FTIR spectra of NR, ENR-17.8, and NRBr-5.1.

Figure 11 ^{1}H NMR spectrum of NRBr-5.1.

the stretching vibration of oxirane rings, and ^{1}H NMR spectrum showed a new signal at 2.72 ppm characteristic of the proton on oxirane ring of epoxidized NR units, similar to the epoxidized model compound. ^{1}H NMR spectrum, was used to determine the percentage of epoxide ring on the modified NR [eq. (2) in Experimental]. In this study, NR was transformed into ENR containing 17.8% of epoxidized units (**ENR-17.8**).

In the second step modification, the addition of **A2** onto epoxide rings of **ENR-17.8** was chosen as it was found earlier that initiator **I₂** is more efficient than the initiator **I₁** for ATRP of MMA. The epoxide

ring opening reaction was carried out in toluene at 110°C for 6 h. The resulting NRBr shows a strong absorption band at 1735 cm^{-1} corresponding to C=O stretching vibration of ester group of bromoalkyl-functionalized NR units as shown on its FTIR spectrum, together with the disappearance of the stretching vibration at 870 cm^{-1} characteristic of oxirane ring of ENR units (Fig. 9). The successful addition of **A2** onto oxirane rings of ENR was also confirmed by ^{1}H NMR spectroscopy, showing important signals at 1.98 and 4.90 ppm corresponding to —C(CH_3)$_2$Br and —C(CH$_3$)(OH)—CH(OC(O)-C(CH$_3$)$_2$Br)—, respectively, together with the quasi disappearance of the signal at 2.72 ppm corresponding to the proton on the oxirane rings (Figs. 10 and 11). The nucleophilic addition of **A2** on the epoxide unit of ENR was schematized in Scheme 5(a). Moreover, the signal of external carbon–carbon double bonds (doublet of vicinal protons at 4.97 ppm, ^{2}J$_{HH}$ = 54 Hz) and —CH(OH)— (multiplet at 4.05 ppm) were also observed. They might come from the rearrangement of oxirane ring of ENR into external allyl alcohol units during the addition of **A2** in the acidic condition [Scheme 5(b)]. In addition, ^{13}C NMR spectrum showed signals at 171, 74.5, and 53.4 ppm corresponding to carbonyl carbon of OC(O)C(CH$_3$)$_2$Br, and carbon of —C(CH$_3$)(OH)—CH(OC(O)C(CH$_3$)$_2$Br) and —OC(O)C(CH$_3$)$_2$Br of bromoalkyl-functionalized NR units, respectively, (Fig. 12). It confirms the occurrence not only the addition product (NRBr) but also external allyl alcohol units by the presence of carbon of carbonyl (—OC(O)C(CH$_3$)$_2$Br) at 171.5 ppm and external carbon–carbon double bond at 109.5 ppm, —C(=CH$_2$)—CH(OH)— and 151.6 ppm, —C(=CH$_2$)—CH(OH)—, respectively.

The integrated area of proton signal in ^{1}H NMR spectrum (Fig. 11) was used to determine the degree of bromoalkyl-functionalized NR units contained in
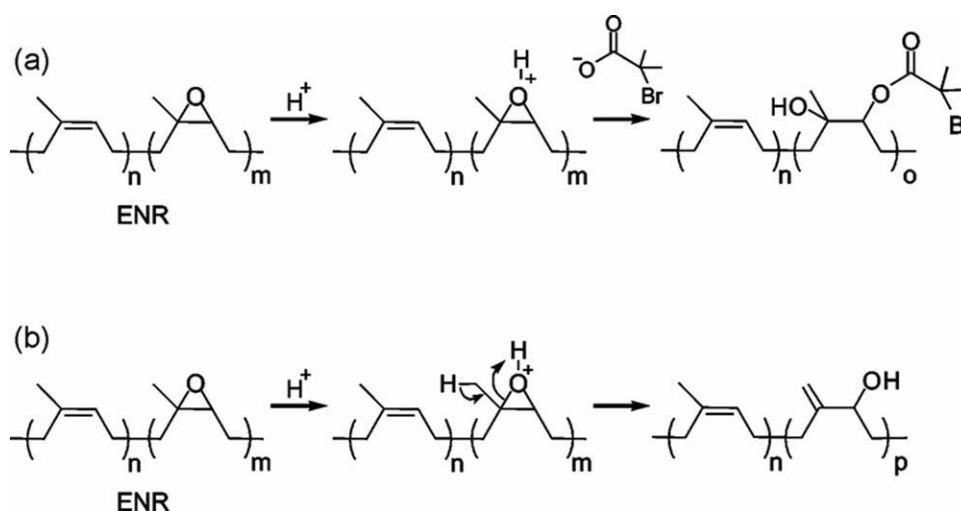
Scheme 5 Mechanisms of (a) nucleophilic addition onto oxirane ring and (b) rearrangement of oxirane ring.
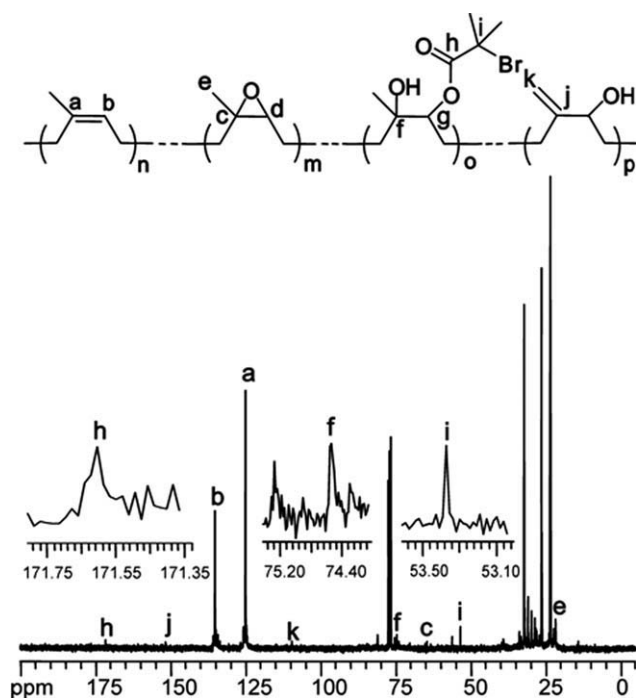
Figure 12 ^{13}C NMR spectrum of NRBr-5.1.

NRBr, the external allyl alcohol units and residual epoxidized NR units from eqs. (3–5) (given in experimental part). For the condition mentioned earlier, **ENR-17.8** gave the content of bromoalkyl-functionalized NR units (NRBr), external allyl alcohol and residual epoxide ring equal to 5.1% (NRBr-5.1), 9.5%, and 3.2%, respectively. No evidence of gelling was found in our condition. The amount of NRBr found on the NR molecular chain is considered to be the amount of grafting sites to be elongated by ATRP of MMA. Generally, the grafting sites generated by the conventional radical system can not be easily determined. It can be highlighted that in our system the amount of grafting sites can be estimated from the percentage of the addition product, which could be easily determined by ^{1}H NMR spectrum.

Synthesis of NR-*g*-PMMA by ATRP of MMA from NRBr macroinitiator

In the graft copolymerization, **NRBr-5.1** was used as macroinitiator to initiate the ATRP of MMA, using Cu(I)Br/NODPMI as a catalytic system. The NODPMI was chosen in this part as it provided considerably narrow PDI for PMMA with the model

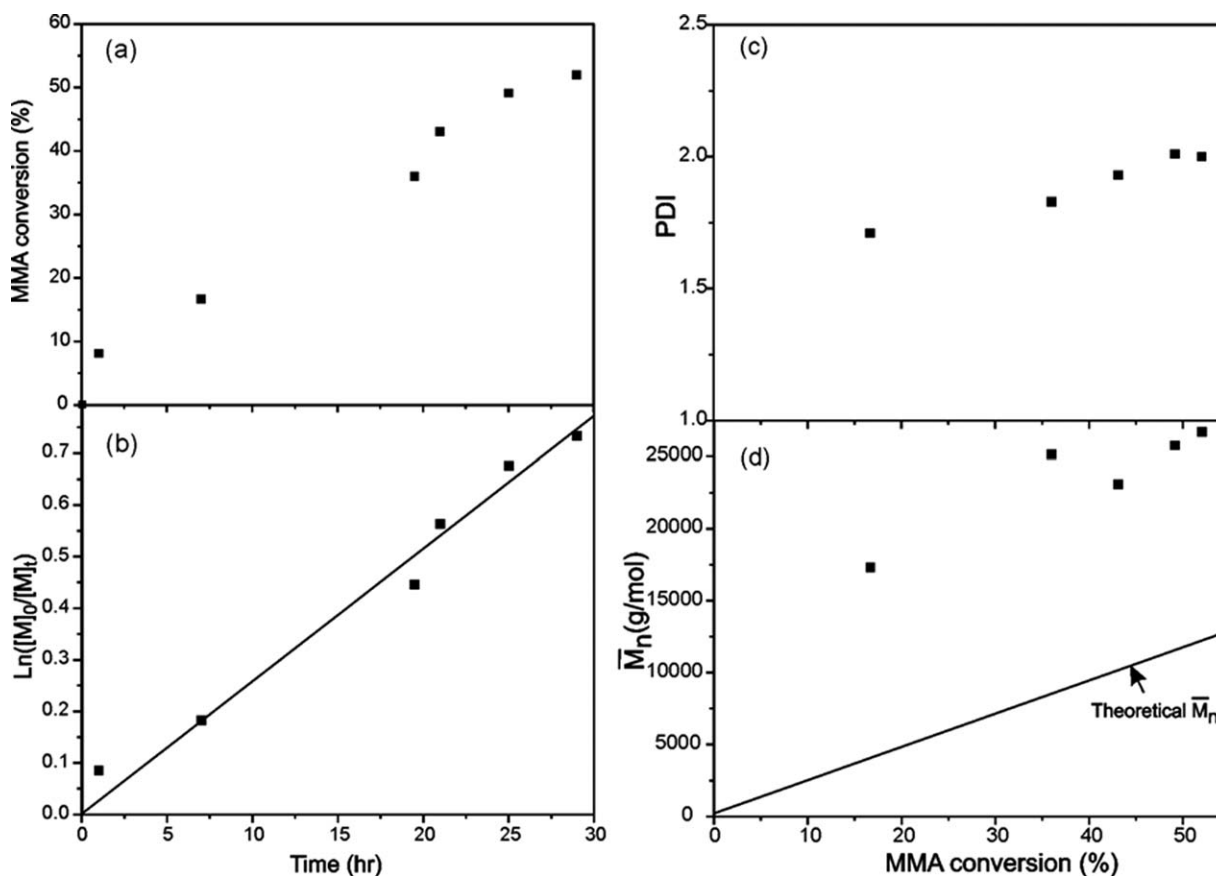**Figure 13** ATRP of MMA initiated from NRBr-5.1 at 90°C in toluene (0.7 wt % of NRBr) in the following conditions: [MMA]/[NRBr units]/[CuBr]/[NODPMI] molar ratios = 220/1/1/2. (a) MMA conversion versus time. (b) First-order kinetic plots. (c) Dependence of PDI on MMA conversion. (d) Dependence of $\overline{M}_n$, determined by SEC, on MMA conversion (%).

investigated earlier. In this part, the study was performed at 90°C using the following molar ratios: [MMA]/[NRBr units]/[CuBr]/[NODPMI] = 220/1/1/2. Figure 10 shows ^{1}H NMR spectrum of NR-*g*-PMMA after purification. The characteristic signal of methoxyl proton of PMMA grafts was found at 3.57 ppm, together with the signal of proton adjacent to carbon–carbon double bond of NR at 5.13 ppm. To study the kinetic of the ATRP of MMA, samples were taken off the reaction mixture at various reaction times to follow MMA conversion by ^{1}H NMR spectroscopy similar to the study with the model compound. The results summarized in Figure 13(a) showed that 52% MMA conversion was obtained after 29 h. The linearity of an internal first order kinetic plot with respect to monomer was observed in the system [Fig. 13(b)]. This could imply the constant concentration of the growing radicals during MMA "grafting from" polymerization.

Thanks to the ester linkages between the PMMA grafts and the NR backbone at the initiating sites, the cleavage of PMMA from the NR main chain was carried out by hydrolysis using trifluoroacetic acid (TFA) (Scheme 4). The PMMA grafts were separated from the TFA treated NR-*g*-PMMA by acetone extraction, then analyzed by ^{1}H NMR. The characteristic proton signals of PMMA similar to Figure 5 were observed without the presence of characteristic signal at 5.13 ppm belonging to the NR. The TFA treated rubber was also analyzed by ^{1}H NMR and the characteristic signal of methoxyl proton of PMMA at 3.57 ppm was not observed. These results confirm that TFA was successfully applied for separation of PMMA from the NR-*g*-PMMA. Then, the molecular weight of the PMMA grafts could be well-determined by SEC, including the PDI. An increase of $\overline{M}_{n,\text{exp}}$ of PMMA grafts isolated with MMA conversion was found as shown in Figure 13(d). The straight line represents the theoretical number–number average molecular weight ($\overline{M}_{n,\text{th}}$) calculated. It was found that $\overline{M}_{n,\text{th}}$ is lower than the $\overline{M}_{n,\text{exp}}$. This may be estimated that some initiating sites on the NR backbone are inactive or fast termination was occurred via intermolecular termination of neighboring chains. The PDI of PMMA grafts was close to 1.7 at low monomer conversion (16.6%) and close to 2 at high MMA conversion (52%) [Fig. 13(c)]. The increase of PDI at higher monomer conversion could come from irreversible terminations between neighboring growing PMMA grafts or by transfer reactions between growing PMMA grafts and NR backbone. This was confirmed by comparing SEC traces of PMMA grafts recovered after hydrolysis reaction of the graft copolymers obtained at different MMA conversions (Fig. 14). A peak with small shoulder was noted when 36 and 52% monomer conversion was analyzed. Beers et al.[24] showed that these side
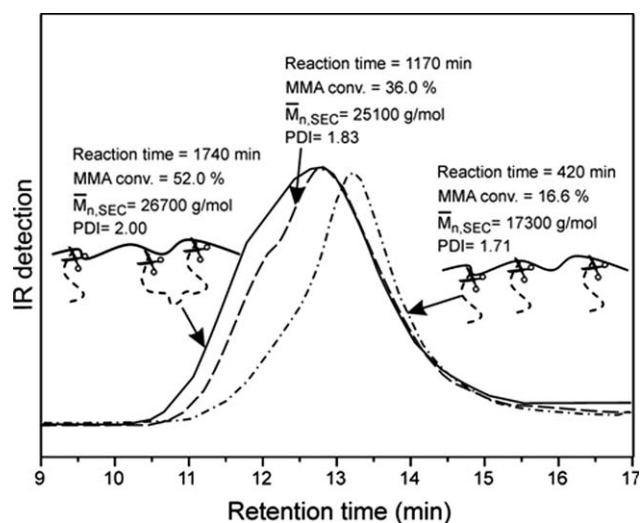

Figure 14 Evolution of SEC traces of PMMA grafts cleaved from NR main chain by hydrolysis, with MMA conversion. ATRP of MMA initiated from NRBr-5.1 at 90°C in toluene (0.7 wt % of NRBr) using [MMA]/[NRBr units]/[CuBr]/ [NODPMI]molar ratios = 220/1/1/2.

reactions are more important at high monomer conversion when the "grafting from" method is used to synthesize densely graft copolymers. It is optimist to propose that the decrease of these side reactions can be occurred in the case that the graft copolymerization is performed in diluted conditions with low amount of initiating units and to stop the reaction at low monomer conversions.

Using our strategy to transform NR into NR macroinitiator by two-step chemical modification, the amount of initiating sites could be determined, hence the amount of grafting sites. Moreover, the molecular size of PMMA grafts could be evaluated after cleavage from the NR backbone. An experimental setup of ATRP of MMA from unmodified NR was also carried out using similar condition as in the case of ATRP of MMA from **NRBr-5.1**. It is not surprising to find that no PMMA grafting on the NR neither PMMA homopolymer was detected as there was not an ATRP initiator in the system.

CONCLUSIONS

Study on functionalization of 4-methyl-4-octene, a model of NR gave successful information that two-step chemical modification i.e., epoxidation and epoxide ring addition with 2-bromopropionic acid (**A1**) and 2-bromo-2-methylpropionic acid (**A2**) could be used to transform the NR into ATRP initiator. The addition of acid **A1** and **A2** on 4,5-epoxy-4-methyloctane (**E**), epoxidized model of NR resulted in formation of *O*-(2-hydroxy-2-methyl-1-(*n*-propyl)pentyl)-2-bromopropionate (**I₁**) and *O*-(2-hydroxy-2-methyl-1-(*n*-propyl)pentyl)-2-bromoisobutyrate (**I₂**), respectively.

The comparison of the ATRP polymerization of the two initiators (I_1 and I_2) and the effects of two different amine ligands i.e., NODPMI and PMDETA, on polymerization rate and polydispersity index (PDI) showed that the modified model I_2 and NODPMI complexed with CuBr were better component than I_1 and PMDETA. These results suggested that acid **A2** should be selected for further study with modified NR.

The two-step chemical modification was successfully applied to transform NR into rubber macroinitiator with **A2**. The amount of **A2** fixation on NR forming bromoalkyl-functionalized NR (NRBr) units determined by ^{1}H NMR was then used to initiate ATRP of MMA. The amount of NRBr was considered to be the amount of PMMA grafting sites. Thank to the ester linkage between PMMA and NR, the PMMA grafts could be cleaved by acid hydrolysis from the NR-*g*-PMMA. Therefore, our strategy resulted in possible determination of the molecular weight of PMMA grafts on the NR-*g*-PMMA by size exclusion chromatography (SEC). While in general, the molecular weight of PMMA grafts created by the conventional radical process have never been reported as the PMMA grafts could not be easily separated from the NR backbone. It was found that ATRP in solution performed at 90°C using the following molar ratios: [MMA]/[NRBr units]/ [CuBr]/[NODPMI] = 220/1/1/2, results in PMMA grafts with PDIs close to 1.7.

References

1. Cooper, W.; Vaughan, G. J Appl Polym Sci 1959, 1, 254.
2. Enyiegbulam, M. E.; Aloka, I. U. J Appl Polym Sci 1992, 44, 1841.
3. Lenka, S.; Nayak, P. L.; Das, A. P.; Mishra, S. N. J Appl Polym Sci 1985, 30, 429.
4. Lenka, S.; Nayak, P. L.; Mohanty, I. B.; Mishra, S. N. J Appl Polym Sci 1985, 30, 2711.
5. Lenka, S.; Nayak, P. L.; Das, A. P. J Appl Polym Sci 1985, 30, 2753.
6. Oliveira, P. C.; Oliveira, A. M.; Garcia, A.; Barboza, J. C. S.; Zavaglia, C. A. C.; Santos, A. M. Eur Plym J 2005, 41, 1883.
7. Oommen, Z.; Thomas, S. J Appl Polym Sci 1997, 65, 1245.
8. Matyjaszewski, K. Controlled Radical Polymerization: ACS Symposium Series 685; Washington DC: American Chemical Society, 1998.
9. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921.
10. Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689.
11. Fettes, E. M. Chem Reaction of Polymers. Wiley: New York, 1964.
12. Wang, X. S.; Luo, N.; Ying, S. K. Polymer 1999, 40, 4515.
13. Coiai, S.; Passaglia, E.; Ciardelli, F. Macromol Chem Phys 2006, 207, 2289.
14. Phinyocheep, P.; Duangthong, S. J Appl Polym Sci 2000, 78, 1478.
15. Derouet, D.; Brosse, J. C.; Challioui, A. Eur Polym J 2001, 37, 1315.
16. Haddleton, D. M.; Jasieczek, C. B.; Michael, J. H.; Shooter, A. J. Macromolecules 1997, 30, 2190.
17. Limer, A.; Haddleton, D. M. Eur Polym J 2006, 42, 61.
18. Xia, J.; Matyjaszewski, K. Macromolecules 1997, 30, 7697.
19. Phetphaisit, C. W.; Phinyocheep, P. J Apply Polym Sci 2003, 90, 3546.
20. Burguière, C.; Pascual, S.; Bui, C.; Vairon, J. P.; Charleux, B. Macromolecules 2001, 34, 4439.
21. Nanda, A. K.; Matyjaszewski, K. Macromolecules 2003, 36, 599.
22. Ando, T.; Kamigaito, M.; Sawamoto, M. Tetrahedron 1997, 53, 15445.
23. Tang, W.; Matyjaszewski, K. Macromolecules 2006, 39, 4953.
24. Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K. Macromolecules 1998, 31, 9413.