

Original Article

A novel polymeric herbicide based on phenoxyacetic acid derivatives

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Abstract

A novel polymeric herbicide based on phenoxyacetic acid derivatives was prepared by the reaction of epoxidised liquid natural rubber (ELNR) with 2,4-dichlorophenoxyacetic acid (2,4-D) or 2-methyl-4-chlorophenoxyacetic acid (MCPA). The liquid natural rubber (LNR) was firstly obtained from the degradation of natural rubber latex with *tert*-butyl hydroperoxide and cobalt acetylacetone at 65°C for 72 hrs. The epoxidised liquid natural rubber was prepared from the reaction of LNR with formic acid and hydrogen peroxide at 50°C for 6 hrs. The reaction of epoxidised liquid natural rubber with 2,4-D or MCPA using triethylamine as a catalyst in toluene was performed at 70, 80, and 90°C for 6, 9, 12, 18, and 24 hrs. The polymeric herbicides obtained were characterized and the grafting percentage of 2,4-D or MCPA onto liquid natural rubber were also determined by FT-IR and ¹H-NMR spectroscopy. It was found that the grafting percentage increased with increasing amount of reactants, temperature, and reaction time. The release of 2,4-D and MCPA from polymeric herbicides was investigated in pH 6, 7, and 8 buffers at room temperature. The results show that the slowest release of 2,4-D and MCPA was found to be constant at pH 7 for 14 and 10 days, respectively.

Keywords: liquid natural rubber, epoxidised liquid natural rubber, polymeric herbicide, 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid

1. Introduction

Conventional usage of herbicides often results in destruction of non-targets. Controlled release might solve the undesirable side effects, which accompany the use of conventional biologically active agents. Polymeric bioactive agents are of great utility in the controlled release field since they may be tailored for specific applications, such as acrylamide copolymer with structopendent naphthylacetic acid and indoleacetic acid esters (McCormic and Kim, 1988), encapsulation of 2,4,5-trichlorophenoxyacetic acid with starch-*g*-poly(vinyl alcohol) (Zhu and Zhuo, 2001a), 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid with starch-*g*-poly (butyl acrylate) (Zhu and Zhuo, 2001b). Additionally, natural rubber has been used as a polymeric supporter for latex stimulants, such as naphthylacetic

acid (Brosse *et al.*, 1992), and 2,4-dichlorophenoxyacetic acid (Klinpituksa *et al.*, 2000). Although a large number of polymeric bioactive materials have been described, few have been thoroughly studied such as macromolecular structure, mechanism of activity, kinetics of release, and biological activity.

The purpose of this study was to prepare the polymeric herbicides from the reaction of epoxidised liquid natural rubber (ELNR) with 2,4-dichlorophenoxyacetic acid (2,4-D) or 2-methyl-4-chlorophenoxyacetic acid (MCPA) and also to study of 2,4-D and MCPA releasing from corresponding polymeric herbicides.

2. Materials and Methods

2.1 Materials

Natural rubber latex (NRL) with high ammonia content was provided by Pattani Industry Ltd., 2,4-dichlo-

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rophenoxyacetic acid (2,4-D) and 2-methyl-4-chlorophenoxyacetic acid (MCPA) were obtained from Fluka, Switzerland. *tert*-Butyl hydroperoxide and cobalt acetylacetone and triethylamine were obtained from Sigma-Aldrich Chemie, Belgium. Formic acid AR grade was obtained from AnalalR®, England. Hydrogen peroxide and toluene were obtained from Merck Schuchardt, Germany. Sodium dodecyl sulphate was obtained from Riedel-de Haen, Germany. Methanol and sodium hydrogen carbonate were obtained from Merck Schuchardt, Germany.

2.2 Preparation of liquid natural rubber

LNR was obtained by degradation of 20% DRC natural rubber latex with *tert*-butyl hydroperoxide of 0.5 parts per hundred (phr) and cobalt acetylacetone of 1 phr by means of mechanical stirrer in a reaction kettle flask at 65°C for 72 hrs. LNR was precipitated in methanol and then dried in hot air oven at 40°C. Molecular weight of LNR was determined by GPC (Waters 1525, 1717 plus autosampler and waters 2414 reflective index detector) and analyzed by FT-IR (Nicolet MAGNA-IR 560 spectrophotometer).

2.3 Preparation of epoxidised liquid natural rubber

ELNR was prepared by using 10% w/v LNR in toluene. Formic acid and hydrogen peroxide in a ratio of 30:60 (% mol with respect to isoprene unit) were added drop wise and stirred at 50°C for 6 hrs. ELNR was then washed in 5% NaHCO₃ solution, precipitated in methanol and dried at 40°C. ELNR was analyzed by ¹H-NMR (Bruker DPX-300 spectrometer, 300 MHz) and FT-IR spectroscopy and the epoxidation level was calculated.

2.4 Preparation of polymeric herbicides

The polymeric herbicides based on 2,4-D or MCPA were performed by mixing of 0.4 g triethylamine and 4 g 2,4-D or MCPA in 10% w/v of ELNR in toluene in round bottom flask placing in water bath at 70, 80, and 90°C for 6, 9, 12, 18, and 24 hrs. The LNR-g-2,4-D and LNR-g-MCPA obtained were precipitated in methanol and then dried in oven at 40°C. The characterization of polymeric herbicides and the grafting percentage of 2,4-D or MCPA onto liquid natural rubber molecules were determined by FT-IR and ¹H-NMR spectroscopy.

2.5 Herbicide release studies

Samples (5.0 g) was transferred into a beaker containing 100 mL of pH 6, 7, and 8 buffer solution. The beaker was placed on a hot plate at ambient temperature and stirred gently by means of magnetic bar. At desired interval, the solution mixture was drawn out and measured absorbance for determining of 2,4-D ($\lambda_{\text{max}} = 288 \text{ nm}$) and MCPA ($\lambda_{\text{max}} = 222 \text{ nm}$) by means of UV-spectrophotometry. The amounts

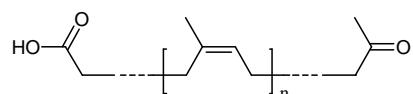
of the herbicides released were calculated from corresponding standard curves.

3. Results and Discussion

3.1 Preparation of LNR

The number-average molecular weight (\overline{M}_n) and the weight-average molecular weight (\overline{M}_w) of LNR using as a starting material for this work were 30,190, and 99,380 g.mol⁻¹ compared to those of original natural rubber, 412,240 and 2,833,380 g.mol⁻¹, respectively. LNR with brown color and low viscosity was obtained by chain scission of isoprene unit of natural rubber in the present of *tert*-butyl hydroperoxide and cobalt acetylacetone. The degradation of natural rubber molecule occurred due to Co²⁺ complexation and *tert*-butyl hydroperoxide formed a radical and then substracted allylic proton from isoprene unit structure of corresponding NR as described previously (Shelton, 1971; Stivala *et al.*, 1983)

Figure 1 shows the FTIR spectrum of liquid natural rubber obtained by the degradation of natural rubber. The absorption bands appear at 3440 cm⁻¹ (OH stretching), 1720 cm⁻¹ (C=O stretching), 1440 cm⁻¹ (C-H bending of CH₂), 1375 cm⁻¹ (C-H bending of CH₃) and 835 cm⁻¹ (=C-H out of plane deformation). We conclude that *tert*-butyl hydroperoxide formed a radical, which further substracted allylic hydrogen of NR to form peroxide in isoprene chain and cleaved the chain to obtain ketone carboxylic chain. The possible structure of LNR obtained is shown as follows:



3.2 Preparation of ELNR

Epoxidation of LNR was carried out by using formic acid *in situ* generated from formic acid and hydrogen

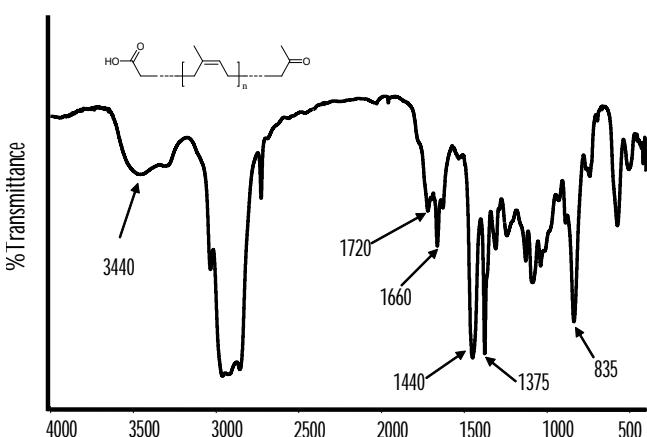


Figure 1. FT-IR spectrum of liquid natural rubber (LNR).

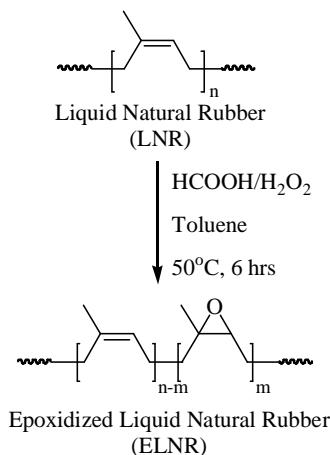


Figure 2. Epoxidation of liquid natural rubber by formic acid and hydrogen peroxide.

peroxide. The epoxidation reaction is shown in Figure 2. FT-IR spectroscopic analysis shown in Figure 3 revealed that the absorption bands of *cis*-1,4-polyisoprene constituent in ELNR appear at 1440 cm⁻¹ (-CH₂- deformation), 1375 cm⁻¹ (methyl C-H deformation) and 835 cm⁻¹ (=C-H out of plane deformation) (Ng and Gan, 1981; Gelling, 1991). The absorptions at 870 cm⁻¹ and 1251 cm⁻¹ can be attributed to the epoxy group.

The ELNR was analyzed by nuclear magnetic resonance spectroscopy, ¹H-NMR (Bruker DPX-300 NMR spectrometer, 300 MHz). Epoxidation lead to a very significant shift of the methyl protons, the disappearance olefinic proton (5.14 ppm) and the appearance of a methine resonance (2.70 ppm) due to the proton attached to the oxirane ring as described previously (Burfield *et al.*, 1984; Bradbury and Perera, 1985) (Figure 4).

The quantitative analysis of mol % epoxy of ELNR obtained at various times was calculated from the two integrated intensity between 2.70 ppm and 5.14 ppm (Burfield *et al.*, 1984). ELNR with 35 mol % epoxy obtained from 6

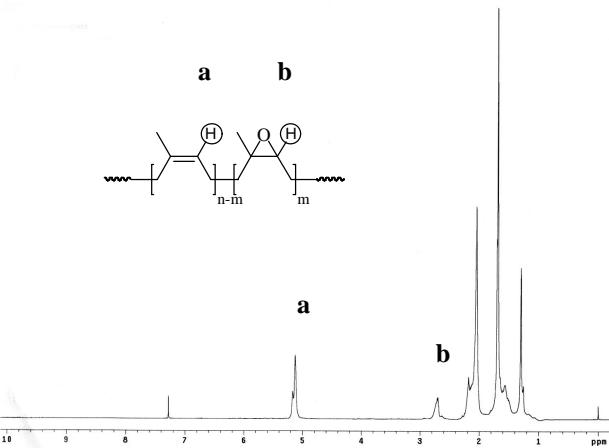


Figure 4. ¹H-NMR signal of epoxidized liquid natural rubber (ELNR) for 6 hrs.

hrs reaction time was chosen for further investigation.

3.3 Preparation of polymeric herbicides

The mechanism for obtaining polymeric herbicides, LNR-g-2,4-D and LNR-g-MCPA, from ELNR and 2,4-D or MCPA in the presence of triethylamine as a catalyst occurred possibly *via* hydrogen bond-triethylamine complex, the same reaction as phenyl glycidyl ether with benzoic acid in the presence of amine (Tanaka, 1967). It is presented in Figure 5.

The grafting percentage of 2,4-D and MCPA onto LNR with reaction time was determined by ¹H-NMR spectroscopy. The experiments performing at 70, 80, and 90°C are shown in Figure 6 and 8. It revealed that the grafting percentage increased with increasing reaction time. The optimum grafting was found to be 4.76% and 5.12% for 2,4-D and MCPA for 18 and 24 hrs, respectively. The grafting amounts of both herbicides onto LNR are nearly similar. It may be due to their similarity of their chemical structures.

The grafting percentage of polymeric herbicides was calculated as follows:

$$\% \text{ Grafting} = \frac{A_{4.71}}{A_{4.71} + 2A_{5.14}} \times 100$$

$A_{4.71}$ = Integration area of $-\text{OCOCH}_2\text{O}-$ in herbicides
 $A_{5.14}$ = Integration area of olefinic hydrogen in natural rubber

Figure 7 and Figure 9 show the ¹H-NMR signal of LNR-g-2,4-D and LNR-g-MCPA, which appear to be corresponding to the olefinic proton (5.14 ppm) and the proton of $-\text{OCOCH}_2\text{O}-$ in herbicide (4.71 ppm).

3.4 Release studies

The influence of various pH on 2,4-D and MCPA released from LNR-g-2,4-D and LNR-g-MCPA is shown in

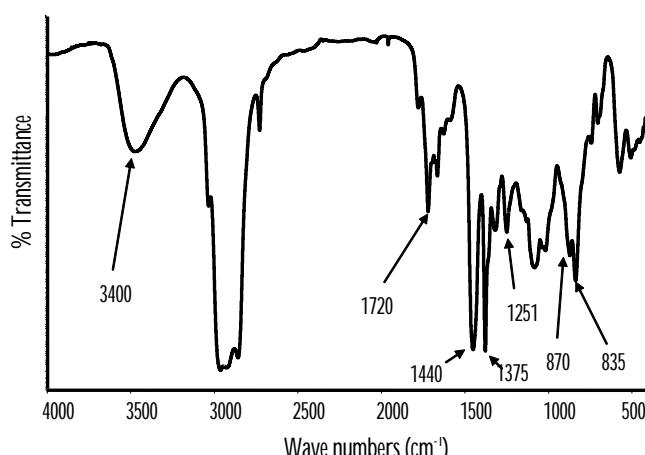


Figure 3. FT-IR spectrum of epoxidized liquid natural rubber at 50°C for 6 hrs.

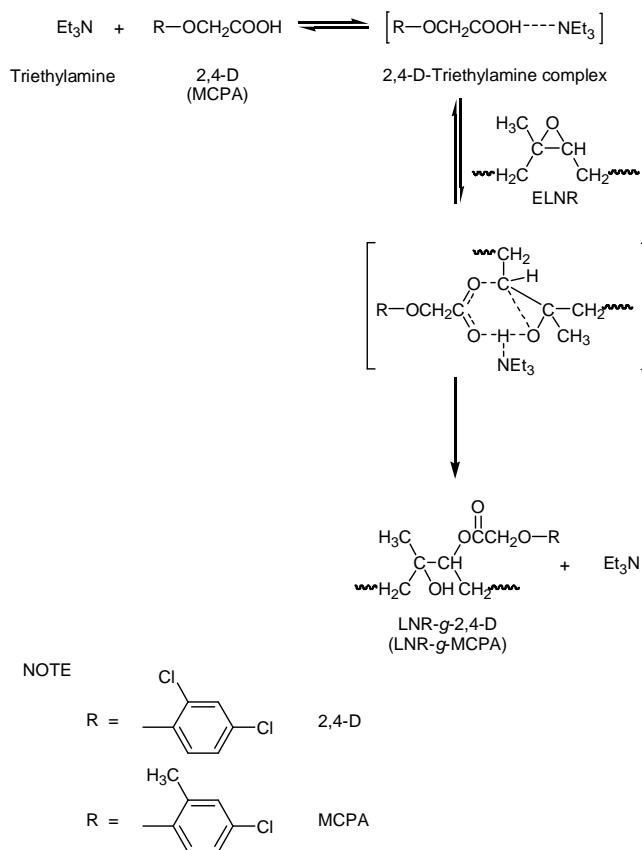


Figure 5. Proposed mechanism of LNR-g-2,4-D and LNR-g-MCPA formations from the reaction of ENR with 2,4-D and MCPA in the presence of triethylamine as a catalyst.

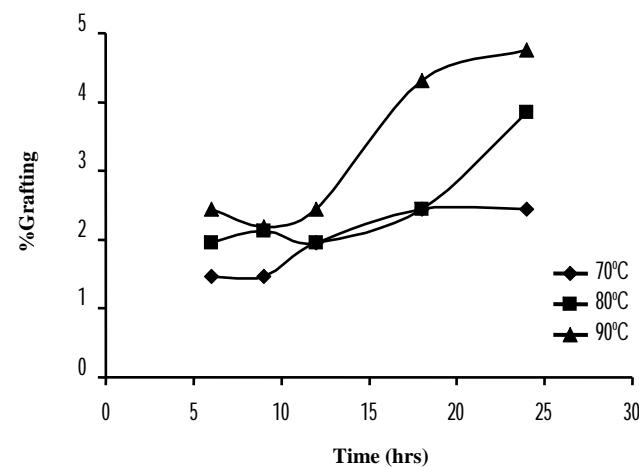


Figure 6. Variation of % grafting of 2,4-D on LNR with times at 70, 80, and 90°C.

Figure 10 and Figure 11, respectively. The optimum release of both herbicides was found at pH 7. It might be due to the hydrolysis of ester bond in the polymeric herbicide in neutral medium was rather slow compared with that in acid or basic medium.

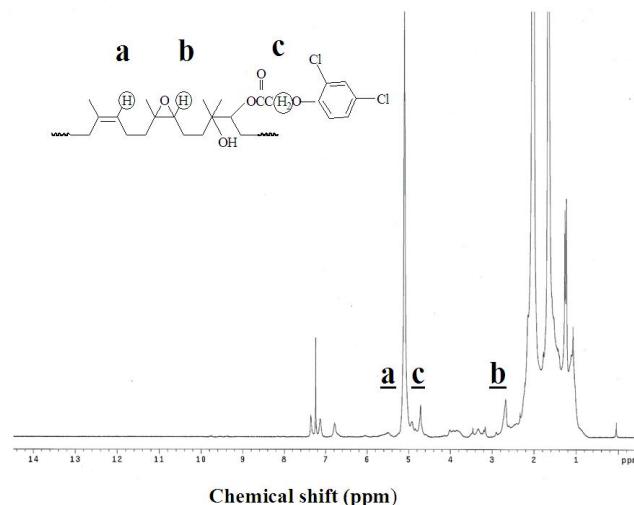


Figure 7. 1H -NMR signal of LNR-g-2,4-D obtained at 90°C for 18 hrs.

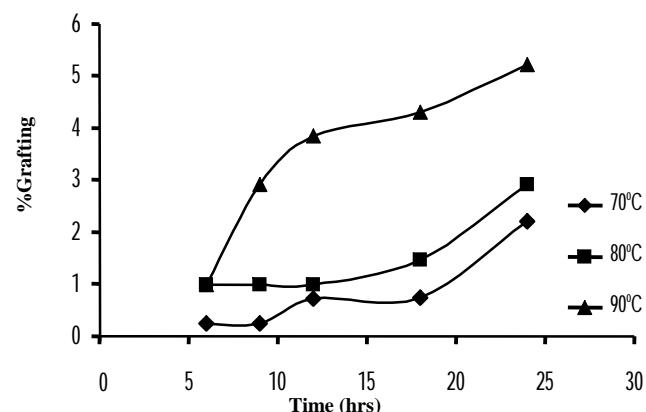


Figure 8. Variation of % grafting of MCPA on liquid natural rubber (LNR) with times at 70, 80, and 90°C.

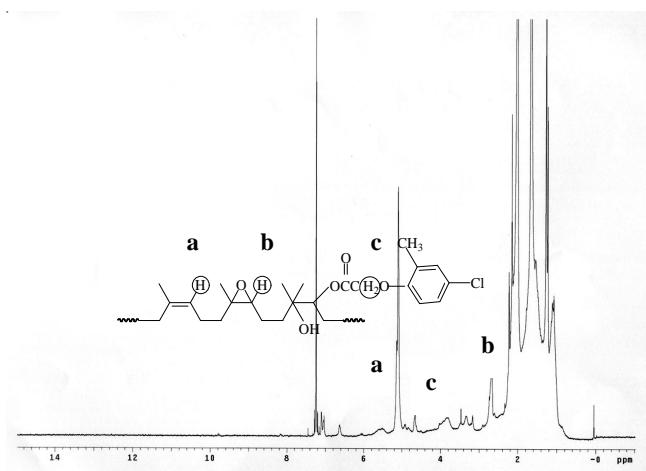


Figure 9. 1H -NMR signal of LNR-g-MCPA obtained at 90°C for 24 hrs.

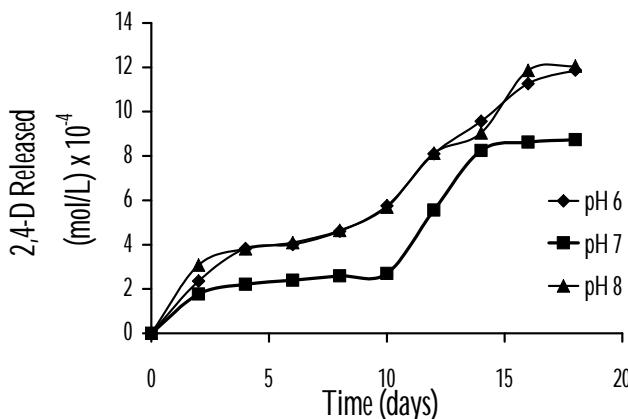


Figure 10. 2,4-D released from LNR-g-2,4-D at pH 6, 7, and 8.

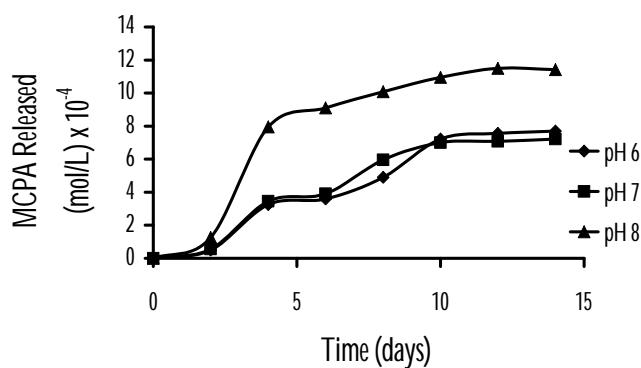


Figure 11. MCPA released from LNR-g-MCPA at pH 6, 7, and 8.

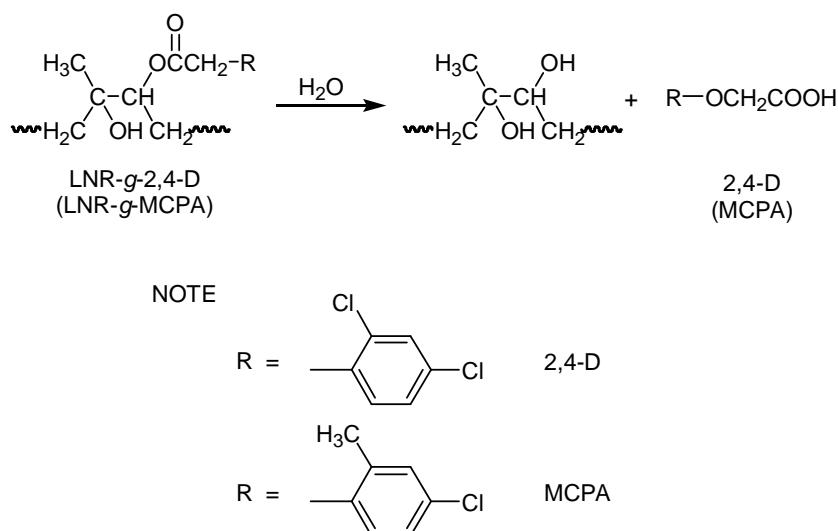


Figure 12. Hydrolysis reaction of polymeric herbicide.

The hydrolysis LNR-g-2,4-D or LNR-g-MCPA for obtaining natural rubber in the form of diol and original 2,4-D or MCPA is shown in Figure 12. The hydrolysis reaction is possibly represented as described in previous work (Soutif *et al.*, 1993).

4. Conclusions

Novel polymeric herbicides were successfully prepared from 2,4-D and MCPA using liquid natural rubber as supporter, which was prior obtained by depolymerization of natural rubber latex in the presence of *tert*-butyl hydroperoxide and cobalt acetylacetone. The optimal grafting of 2,4-D and MCPA onto liquid natural rubber was found to be 4.76% and 5.21% at 90°C for 18 and 24 hrs, respectively. The slow release of both 2,4-D and MCPA from polymeric herbicides, LNR-g-2,4-D and LNR-g-MCPA, *via* hydrolysis reaction of ester bond was found to be the best in pH 7 buffer solution.

Acknowledgements

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