ISSN: 0975-833X

*Available online at http://www.journalcra.com*

*International Journal of Current Research*
*Vol. 9, Issue, 04, pp.49161-49165, April, 2017*

**INTERNATIONAL JOURNAL OF CURRENT RESEARCH**

## RESEARCH ARTICLE

# BIODEGRADABLE POLYMERS OF CELLULOSE BY GRAFTING OF POLYCAPROLACTONE

***,[1]Azam, Mohammad and [2]StephenP. McCarthy**

[1]Institute of Biochemistry, University of Balochistan, Quetta, Pakistan
[2]Biodegradable Polymer Research Centre, Department of Plastic Engineering, University of Massachusetts, Lowell, MA 01854, USA

**ARTICLE INFO**

***Article History:***
Received 20th January, 2017
Received in revised form
12th February, 2017
Accepted 19th March, 2017
Published online 30th April, 2017

***Key words:***

Cellulose and its derivatives, Caprolactone, Biodegradable polymer, Grafting reaction.

**ABSTRACT**

This review paper deals with the biodegradable polymers synthesized by the grafting reactions of caprolactone on to cellulose and its derivatives. A detail study of different methods available in literature for the synthesis of new biodegradable polymers of cellulose and its derivatives by grafting of polycaprolactone are discussed.

***Copyright©2017, Azam, Mohammad and StephenP. McCarthy.*** *This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

**Citation: Azam, Mohammad and StephenP. McCarthy, 2017.** "Biodegradable polymers of cellulose by grafting of Polycaprolactone", *International Journal of Current Research*, 9, (04), 49161-49165.

## INTRODUCTION

Interest in biodegradable polymers has increase in the recent years, due to environmental awareness. A few of these biodegradable polymers are commercially available, but their use is still uncommon due to high cost of these materials. Many researchers are still looking, for new low cost biodegradable polymers. Biodegradable polymers, based on natural material are preferred, because of two major advantages, first they are widely available in nature, so their cost is comparatively less and second due to known biodegradable properties, it is likely that the resultant material would also be biodegradable. Cellulose is a biopolymer, it is synthesized by plants, trees and also synthesized by the bacteria. In these forms, cellulose is highly crystalline due to extensive hydrogen bonding. Because of this behavior, cellulose is infusible and insoluble in most of the organic solvents. Many attempts were made to derivatised cellulose and as a result, many derivatives of cellulose had been developed, which had high impact strength, good solubility and better to process able (Kennedy *et al*., 1985). However, a control derivatization of cellulose is required. It has been suggested that, if at least one hydroxyl group in each repeating units in cellulose is substituted, the modified cellulose will not be degraded by microorganism (Lenz, 1993). Cellulose is Composed of numerous D-glucopyranside repeating units. These units are linked together, by acetal bonds formed between the hemiacetal carbon atom, C1 of the cyclic glucose structure in one unit and a hydroxyl group at C3 (Lenz, 1993). The hydroxyl groups on the glucopyronside ring are vulnerable to the chemical reaction. The non-bonding electron on the hydroxyl group makes it reactive towards electron deficient reagents. Cellulose has three hydroxyl groups per repeating unit. They are in position 2, 3 and 6. The hydroxyl groups at position 2 and 3 are secondary hydroxyl groups, whereas position 6 is a primary hydroxyl groups. The hydroxyl groups at position 2 and 3 are more acidic compared to 6. Therefore, are more reactive towards elecetophilic reagents (Young and Rowell, 1986). A verity of reagents had been used, to react with these hydroxyl groups and to synthesize the new cellulose derivatives. The first derivative of cellulose was known when in 1846 Schonbein discovered the cellulose nitrate (Warth*et al*., 1997), and then in 1869 Schutzenburger made cellulose acetate (Simon *et al*., 1998), further in 1892 Cross & Bevan, discovered that cellulose can be converted into xanthate, which could be regenerated to cellulose in fiber form. In 1908 Dreyfus & Lilienfield, discovered the cellulose ether derivatives and then in 1930 Hill and Jackson (Kennedy *et al*., 1985) reacted urea with cellulose to form cellulose carbamate, and afterward enormous work had begun to derivatized cellulose and to developed new materials for industrial use. Still there is need, to investigated new cellulose derivatives.

***Corresponding author:*** **Azam, Mohammad**
Institute of Biochemistry, University of Balochistan, Quetta, Pakistan.

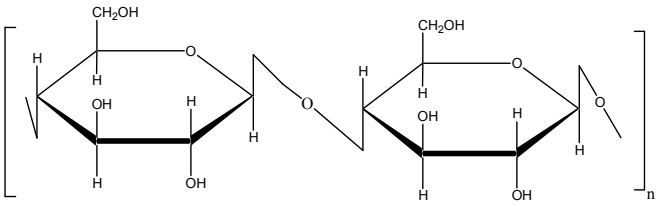

**Fig.1. Structure of Cellulose**

In the recent years when mankind had faced the environmental constrains, once again researchers are focusing on the synthesis of biodegradable polymers based on cellulose and its derivatives. A common approach to synthesized biodegradable polymer based on cellulose is to generate biodegradable branches on to it by grafting reactions. Polycaprolactone has been grafted onto cellulose and its derivatives to develop such biodegradable material. Polycaprolactone (PCL) is a linear aliphatic semicrytalline ester. It is recognized as one of the few synthetic polymer which is biodegradable. The polymer is hydrolyzed by microorganism at the ester linkage (Goldberg, 1995). Its biodegradability has been confirmed in aerobic soil burial, compost and respirometry studies (Goldberg, 1995). Despite being biodegradable PCL has the ability to be fabricated into useful articles by using conventional processing equipment such as injection molding and extrusion. PCL is soluble in a variety of solvents, such as benzene, toluene, methylene chloride, carbon tetracholide THF and cyclohexane and has ability to blend with a variety of other polymers over wide compositional range (Paul and Newman, 1978). High molecular PCL with $T_g$ of 60 $^0$C is a strong ductile polymer with good mechanical strength (Biodegradable polycaprolactone resin, 1994). These properties make it easily processable.

Having such properties attempts were made to blend PCL with cellulose and its derivatives to utilized cellulose and its derivatives as industrial biodegradable polymer. Since cellulose and its derivatives are hydrophilic in nature and PCL is hydrophobic in nature, when they were blended it forms incompatible blends (Olabisi*et al*., 1979). The chemical modification of cellulose and its derivatives by the use of graft copolymerization is one possible way to have biodegradable material with a diverse range of physical properties. The ring opening polymerization of caprolactone in presence of hydroxyl groups provides an easy method to synthesized polyester. Cellulose and its derivatives contain readily available hydroxyl groups and a small amount of suitable catalyst will copolymerized it onto them. The resultant modified cellulose will have utility as biodegradable polymer for industrial use. In order to synthesize new cellulose biodegradable polymer cellulose derivatives are used, due to their solubility in the common organic solvent because of that a homogenous reaction on to cellulose is not possible. In some cases cellulose fiber is used in solid state and grafted with caprolactone. In most case cellulose derivatives, such as cellulose acetate, cellulose hydroxyl ethyl cellulose, and ethyl cellulose are use. One of the common approach is to react the hydroxyl groups on the cellulose and its derivatives and to synthesize the new material having the biodegradable properties.

These hydroxyl groups on the cellulose and its derivatives have been use to regenerate the polymer chain either by the free radical or ionic mechanism. Having, a lot reported work (Ishikura and Matsumoto, 1986; Daicel, 1982; Onishi *et al*., 1985; Ohga and Namikoshi, 1985; Bayer and Dutch Pat, 1980; Asami and Matsumoto, 1985; Yoshioka and Mariko, 2006; Wang *et al*., 2006; Shiraishi *et al*., 1999; Hatakeyama *et al*., 1999) the interest has been directed to prepared cellulose based biodegradable polymers. The purpose this paper is to review the work done for the synthesis of cellulose biodegradable polymers by the grafting of polycaprolactone. Below are the details of biodegradable polymer prepared from the cellulose and caprolactone by such grafting reactions are discussed.

**Biodegradable graft copolymers of cellulose acetate and caprolactone**

Cellulose acetate is widely used for the synthesis of such, biodegradable polymers because, cellulose acetate has good mechanical strength and solubility in common organic solvents. However, cellulose acetate is difficult to process due to high viscosity and high glass transition temperature which effect its industrial application (Zugenmaier, 2004). To utilize cellulose acetate it is usually plasticize with aliphatic and aromatic esters (Lee and Shiraishishi, 2001; Guruprasad and Shashidharar, 2004; Warth *et al*., 1997), this external plasticizer can easily displaced from cellulose acetate causing environmental and health hazard. Cellulose acetate can be utilized as a processable biodegradable polymer after grafted with long chain polycaprolactone. The resultant material has the desire properties and no health hazard as compared to the low molecular weight plasticized cellulose acetate(Lee and Shiraishishi, 2001; Warth *et al*., 1997). The common approach to generated PCL branches from free hydroxyl groups on the cellulose acetate is by the use of Ring Opening Polymerization (ROP). This polymerization method gives well defined grafted structure, with minimum contamination of homopolymer and products with high molecular with products (Albertsson and Verma, 2001). Organometallic catalyst such as $Sn(Oct)_2$ is widely used because of following advantages: a) It is easily reactive in the ROP of CL with hydroxyl substrate. b) it has minimum transesterification reaction. c) it generates high molecular weight product. d) it gives high yield. e) it has minimum toxicity (Dech-Cabaret *et al*., 2004; Deng *et al*., 2005; Rieger *et al*., 2005; Kowalski *et al*., 2005). The mechanism of Sn II $(Oct)_2$ catalyzed reaction has been studied exclusively by kricheldrof (Kricheldorf and Eggerstedt, 1998; Kricheldorf *et al*., 1995). The Sn II$(Oct)_2$ works efficiently at high temperature and in the absence of solvent. Termato and coworker (Teramoto *et al*., 2005) had prepared well define graft product of CA-g-PCL using Sn II octeate. The molecular structure of grafted product was controlled by the reaction time. They observed that the solvent depressed the activity of the CL monomer. The resultant modified CA product obtained with improved mechanical strength and better processability. Videki *et al*. (2005) grafted CA with CL in an internal mixer at temperature between 220$^0$C and reaction time between 5 and 45 minutes in the presence of Sn II octanoate as catalyst. Their results showed that significant modification did not occur at low temperature, below 180$^0$C. The grafting efficiency increased with increasing temperature and time. The grafted product obtained had plasticized the CA which results in a considerable decrease of its glass transition temperature.

Another way to generated grafted branches from the CA backbone first to generated branches from the free OH of CA with terminal reactive group and to condensed it with prepared polymer with reactive polymer via condensation reaction.

Huang and *et al*. (2003) used this approach of non-ionic grafting onto method. Isocyanate terminated PCL was prepared by the reaction of PCL with toluene-2, 4 diisocyanate (TDI), which was further reacted with CDA. The flow temperature of graft copolymers was lower than that of CDA and decreased with increasing, the grafting percentage. Outdoor soil burial test and active sludge tests indicated that the graft copolymer have good biodegradability in natural conditions.

**Cellulose Hydroxy propyl graft poly caprolactone**

Hydroxy propyl cellulose (HPC), is another important cellulose derivative, prepared by the reaction of propylene oxide onto cellulose. HPC has variety of applications (Cai *et al*., 2003; Sanders *et al*., 1986; Shinichi *et al*., 1999; Suzuki and Makino, 1999). HPC is water soluble and has application as base excipient for topical and oral formulation, because of its low oral toxicity, high viscosity in aqueous dispersion thermoplasticity and surface activity (Wang *et al*., 2006). A graft copolymer of HPC and PCL will have improved properties and can have many applications as biodegradable polymers. HPC has poor solubility in common organic solvent due to that CPL grafted onto HPC either in bulk or the derivates of HPC are used. Shi & Burt (2003) synthesized the HPC-graft-PCL in bulk without using, any catalyst, in a sealed tube under nitrogen blanket, placed in an oil bath at 150 $^{o}$C for 24 hours. They observed that in absence of catalyst grafted product has shorter PCL side chains. The ratio of HPC and CL is very important in such reaction. A ratio of 1:4 gave 71 % conversion of CL and 62.8 % yield and in larger scale (30fold), conversion and yield decreased to 61.8% and 56.7 % respectively. Since HPC has poor solubility in common organic solvent an effort have been made to further derivitise the HPC to get more soluble and better chemical reactivity. Wang and coworkers (Wang *et al*., 2003) derivatized the HPC with trimethyl silayl (TMS). They observed that the resultant TMS-HPC has good solubility in organic solvent and improved thermal stability. Another advantage of this TMS-HPC is that it contained easily deprotected TMS group which can have many synthetic applications. A graft copolymer of TMS-HPC grafted PCL was prepared in xylene using Sn II $(Oct)_2$ catalysts the polymerization was conducted under nitrogen at 120 $^{0}$C for 24 hours. The graft copolymer contains hydrophobic PCL side chains and HPC hydrophilic backbone and could be use as suitable carrier for hydrophobic drugs.

**Ethyl cellulose graft polycaprolactone**

Ethyl cellulose (EC) possess good solubility in common organic solvents and has good biocompatibility, high mechanical intensity and stability (Yuan*et al*., 2007). CL grafted onto EC in xylene using Sn $(Oct)_2$ catalyst at 120 $^{o}$C for 24 hours. Various graft copolymers were synthesized by adjusting the molar ratios of the CL monomer to EC. The thermal stability of EC-g-PCL with short PCL branches was poorer than that of linear PCL and EC-g-PCL with long PCL branches. The EC-g-PCL was biodegradable in vitro (Yuan *et al*., 2007). Li and coworkers (1999) used a new approach to prepared hydrophobic-hydrophilic biodegradable polymer containing CL and Hydroxy ethyl cellulose (HEC) backbone. HEC an organic solvent insoluble cellulose, when deposited as a film grafted with caprolacone in bulk using and enzyme lipase derived from porcine pancreas (PPL) and from a thermophilic CLONENZYME ESL-001. The reaction resulted in CL grafted HEC with DSs between 0.10 and 0.32 in terms of per anhydrous glucose unit. Jiang and coworkers (Jiang*et al*., 2011) had grafted ε-CL on the HEC by homogenous ring-opening graft copolymerization and deprotection procedure. In this procedure first hydroxyl groups of HEC was partially protected by hexamethyldisilzane as silylated agent before grafting.

**Cellulose or Cellulose fiber graft polycaprolactone**

As discussed earlier due to insolubility it difficult to modified cellulose by homogenous polymerization. Most of the reaction done to modify cellulose is either on cellulose in solid state or on cellulose fiber. However, Mayumi and coworkers (Mayumi *et al*., 2006) used special solvent system of LiCl/N, N-dimethylacetamide to performed the homogenous polymerization of CL onto cellulose. CL was polymerized in Cellulose/LiCl/DMAc solution at 128 $^{o}$C under $N_2$ atmosphere for 12 hours. The ring opened CL moiety was selectively introduced at the C6-OH of Cellulose molecule. Cellulose-g-PCL with low degree of substitution was soluble in some organic solvents such as DMSO. Cellulose fiber is used as reinforcement material in biocomposite. To improve the biocompatibility of cellulose fiber chemical modification cellulose fiber with deferent reagents has been done (Lonnberg *et al*., 2006). Hult and coworkers (Lonnberg *et al*., 2006; Lonnberg *et al*., 2011) grafted PCL directly onto solid cellulose substrate using benzyl alcohol initiator, Sn $(Oct)_2$ catalyst and toluene as solvent. Reaction was carried out at 95 $^{o}$C for 18-20 hours under argon. The conversion was 98-100 %. Cellulose substrate was grafted with different graft length i.e DP 330 and DP 125. After the reaction morphology of the paper was changed and has become much smoother. Hafren and Cordova (Hafren and Cordova, 2005) were the first researchers who had modified the cellulose fiber with nonmetallic catalyst, an organic acid. They successfully modified the what man filter paper and cotton with CL using tartaric acid as catalyst in bulk at 120 $^{o}$C for 6 hours. The mild reaction conditions and the nontoxic chemicals can leads to a new inexpensive biocompatible cellulose-g-PCL synthesis. Labet & Thielemans (2011 & 2012), had performed the surface modification of cellulose nanocrystals by ring opening polymerization of ε-caprolactone without catalyst and with citric acid as catalyst.

**Conclusions**

Cellulose and its derivative can be grafted with PCL to synthesized cellulose based biodegradable polymers. The organometallic Sn II $(Oct)_2$ is good catalyst for such grafted reaction. It can be used in solution and in bulk. However, the solution polymerizations give low molecular branches and on the other hand bulk polymerization gives high molecular branches. Polycaprolactone can be grafted onto Cellulose in fiber, and in paper form using Sn II $(Oct)_2$ catalyst. The resultant graft material has biodegradable properties and improved processibility and mechanical strength of cellulose and its derivatives.

## REFERENCES

"Biodegradable poly (caprolactone) resin, 1994. TONE® Polymers P-767 & P-787, Union Carbide Corp., Specialty polymers & products.

Albertsson, A-C; Verma, K.I; 2002. Polyesters: synthesis, properties and applications. *Advances in Polymer Science*, Vol. 157, 1-40.

Asami, A, & Matsumoto, Jpn. Pat. 80221,476 (1985) (to Daicel chem. Ind.)

Bayer AG, Dutch Pat. 3,048,697, A1 (1980).

Cai, T; Hu; Z, B; Ponder, B; John, J, St; Moro, D; 2003. Synthesis and study of controlled release from nanoparticles and their networks based on functionalized hydroxypropylcellulose. *Macromolecules,* 36, 6559.

Daicel chem..*Ind, Jpn Pat*, 5,986,621 1982.

Dech-Cabaret, O; Martin-Vaca, B; Bernaerts, K.V; Du Prez, F.E; Jerome, C; 2004. Controlled ring opening polymerization of lactide and glycolide. *Chem. Rev*., 104, 6147-6176.

Deng, C; Rong, G.Z; Tian, H.Y; Tang, Z.H; Chen, X, S; Jing, X.B; 2005. Synthesis and characterization of poly(ethylene glycol)-*b*-poly (L-lactide)-*b*-poly(L-glutamic acid) triblock copolymer. Polymer 46, 653-659.

Goldberg, D. 1995. A review of the biodegradability and utility of poly(caprolactone)*Journal of Environmental Polymer Degradation*, Vol. 3, No. 2, 61-67

Guruprasad, K.H; Shashidharar, G.M. 2004. Grafting, blending, and biodegradability of celluslose acetate. *J Appl. Polym. Sci*; 91 (3) 1716-23.

Hafren, J; Cordova, A; 2005. A direct organocatalytic polymerization from cellulose fibers. *Macromol. Rapid commun*., 26, 82-86.

Hatakeyama, Hyoel; Hirose Shigeo (Agency of Industrial Science & Tech, Japan). (1999) Pat. JP 11071401.

Ishikura, M. and Matsumoto, jpn. Pat. 60, 221. 476 (1986) (to Daicel chem. Ind).

Jiang, C; Wang, X; Sun, p; Yang, C; 2011. Synthesis and solution behavior of poly(caprolctone) graft hydroxylethyl cellulose copolymers. *International Journal of Biological Macromolecules*, 48, 210-214.

Kennedy, J.F; Philips, G.O; Wedlock, D.J and William, P.A; Cellulose and its derivatives. Ellis Horwood Limited, Chichester, England. 1985.

Kowalski, A; Libiszowski, J; Biela, T; Cypryk, M; Duda, A; Penczek, S; 2005. Kinetic and mechanism of cyclic ester polymerization initiated with tin (II) octoate. Polymerization of ε- caprolactone and L, L-Lactide co-initiated with primary amine. *Macromolecules*, 38, 8170-8176.

Kricheldorf, H, R; Eggerstedt, S; 1998. Macrocycles 2. Living macrocyclic polymerization of ε- caprolactone with 2,2-dibutyl-2-2stanna-1,3-dioxepane as initiator. *Macromol. Chem. Phys*., 199, 289-290.

Kricheldorf, H, R; Saunders-Kreiser, I; Boettcher, C; 1995. Polylactone 31. Sn (II) octoate-initiated polymerization of L-lactide: a mechanistic study. *Polymer*, Vol.36 No. 6, pp 1253-1259.

Labet, M; Thielemans, W; 2011. improving the reproducibility of chemical reactions on the surface of celluslose nanocrystals: ROP of ε-caprolactone as a case study. *Cellulose*, 18, 607-617.

Labet, M; Thielemans, W; 2012. Citric acid as a benign alternative to metal catalysts for the production of cellulose-grafted-polycaprolactone copolymers. Polymer Chemistry, 679-684

Lee S.H; Shiraishishi, N; 2001. Plasticization of cellulose diacetate by reaction with maleic anhydride, glycerol and citrate ester during melt processing. J. Appl. Polym Sci; 81 (1); 243-250.

Lenz, R. W; 1993. Biodegradable Polymers. Advances in Polymer Science, Vol. 107, 1-40.

Li, J; Xie, W; Cheng, H, N; Nickol, R, G; & Wang, G, P; 1999. Polycaprolactone-modified hydroxylethyl cellulose films prepared by lipase-catalystzed ring-opening polymerization. Macromolecules, 32, 2789-2792.

Lonnberg, H; Fogelstrom, L; Zhou, Q; Hult, A; Berglund, L; Malmstrom, E; 2011.. Investigaation of the graft length impact on the interfacial toughness in a cellulose poly (epsilon-caprolactone) bilayer laminate. *Composite Science & Technology*, 71, 9-12.

Lonnberg, H; Zhou, Q; Brumer, H; Teeri, T, T; Malmstron, E; & Hult, A; 2006. Grafting of cellulose fibers with (poly caprolactone) and poly(lactic acid) via ring opening polymerization. *Biomacromolecules*, 7, 2178-2185.

Mayumi, A; Kitaoka, T; Wariishi, H; 2006. Partial substitution of cellulose by ring-opening esterification of cyclic esters in a homogenouse system. *Journal of Applied Polymer Science*, Vol. 102, 4358-43-64.

Ohga, A; & Namikoshi, H, Br. Pat. 2,152,944 1985. (Daicel chem. Ind)

Olabisi, O, Robeson, L.M. and Shaw, M.T, eds, 1979. Polymer-Polymer Miscibility, Academic press Inc., New York, 1-20.

Onishi, M; Takahashi, S, Namikoshi and Asami, M, Jpn, Pat. 60,188,401 1985. (Daicel chem. Ind.)

Paul, D.R and Newman, S; eds., 1978. Polymer blends, Vol. 2. Academic Press, New York.

Rieger, J; Coulembier, O; Dubois, P; Bernaerts, K,V; Du Prez, F.E; Jerome, C; 2005. Controlled Synthesis of an ABC Miktoarm Star-Shaped Copolymer by Sequential Ring-Opening Polymerization of Ethylene Oxide, Benzyl β-Malolactonate, and ε-Caprolactone. *Macromolecules*, 38, 10650-10657.

Sanders, J, C; Breadmore, M,C; Kwok, Y, C; Horsman, K, M; Landers, J, P; 2003. Hydroxypropyl Cellulose as an Adsorptive Coating Sieving Matrix for DNA Separations: Artificial Neural Network Optimization for Microchip *AnalysisAnal. Chem*., 75 (4), 986-994.

Shi, R; Burt, M; 2003. Synthesis and charachterization of amphiphilic hydoxypropylcellulose-graft-poly(ε-caprolactone). *Journal of Polymer Science*, Vol. 89, 718-727.

Shinichi, S; Miyoko, I; 1999. Change in handedness of cholesteric liquid crystal during swelling in water for crosslinked hydroxypropyl cellulose films filled with cellulose powders. *Polymer,* 40, 2455-2457.

Shiraishi, Nobuo; Yoshioka, Mariko; Kozeki, Eiichi; Inozuka Akihiro. (Shimadzu Corp; Japan; Daicel Chemcial Indus) 1999. Polylactone-grafted cellulosic polymers and their manufacture. Pat. JP 11255870.

Simon, J, Muller, H.P, Koch, R and Muller, V. 1998. Thermoplastic and biodegradable polymers of cellulose. *Polymer Degradation & stability*, 59, 107-115.

Suzuki, Y; Makino, Y; 1999. Mucosal drug dlivery using cellulose derivates as functional polymer. *Journal of Control Release,* 62, 101-107.

Teramoto, Y; Ama, S; Higeshiro; Nishio, Y; 2004. Cellulose acetate-graft-poly(hydroxyl alkanoate)s: synthesis and dependence of the thermal properties on copolymer composition. Macromolecular Chemistry & Physics, Vol. 205, Issue 14, 1904-1915.

Videki, B; Klebert, S; Pukanszky, B; 2005. Grafting of caprolactone to cellulose acetate by reactive processing. European polymer Journal, 41, 1699-1707.

Wang, C; Dong, Y; Tan. H; 2003. Biodegradable: Brushlike graft polymers. Polymerization of caprolactone onto water-soluble hydroxypropyl cellulose as the backbone by the

protection of the trimethylsilyl group. Journal of Polymer Science: part A: Polymer Chemistry, Vol. 41, 273-280.

Wang, C; Tan, H; Dong, Y; & Shao, Z; 2006. Trimethyl silyl hydoxylpropyl cellulose: preparation, properties and as precursor to graft copolymerization of ε-caprolactone. Reactive & Functional Polymers 66, 1165-1173.

Wang, Cai-qi; Tan, Hui-min, Dong, Yu-ping; Li, Guang-tao, 2006. Properties of amphiphilic biodegradable copolymer the hydroxypropyl cellulose-graft-polycaprolactone. Gaofenzi Cailliao Kexue Yu Gongcheng 22 (1), 123-126

Wang, D; Xuan, Y; Huang, Y; & Shen, J; 2003. Synthesis and properties of graft copolymer of cellulose diacetate with poly(caprolactone monoacrylate). Journal of Polymer Science, vol. 89, 85-90

Warth, H, Mulhaupt, R, and Schatzle, J; 1997. Thermoplastic cellulose acetate and cellulose acetate compounds prepared by reactive processing.J. Appl. Poly. Sci., 64: 231-242.

Yoshioka, Mariko, 2006. (Agri Future Joetsu Co, Ltd, Japan), Pat. WO 2006048946.

Young, R. A. and Rowell, R. M. 1986. Cellulose structure, modification and hydrolysis, Page 113, John Wiley & Sons Inc. New York.

Yuan, W; Yuan, J; Zhang, F; & Xie, X; 2007. Synthesis, characterization and in vitro degradation of ethyl cellulose-graft-poly(ε-caprolactone)-block-poly(l-lactide) copolymers by sequential ring-opening polymerization. Biomacromolecules; 8(4): 1101-8.

Zugenmaier, P; 2004. Characteristics of cellulose acetate: characterization and physical properties of cellulose acetate. Macromol. Symp; 208; 81-166.

*******