

## Syntheses of Cellulosic Graft Copolymers

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### Abstract

Cellulosic graft copolymers were synthesized to use them as the functional materials. Three methods containing atom transfer radical polymerization (ATRP), macro-azo-initiator (MAI) method, and the polymerization catalyzed by tetrabutylammonium fluoride (TBAF) were performed in this work.

### Introduction

Cellulose is the most plentiful natural polymer and is present in various plants, microorganisms and animals. The natural abundance of cellulose and a number of attractive properties such as renewable, biodegradable, film- and fiber-forming properties appear to make it a suitable substrate for functionalization.

So far, a number of studies have been reported for the graft polymerization of vinyl or cyclic monomers onto various materials. Recently, structure-controlled graft copolymers have been synthesized using ATRP<sup>1</sup>, MAI<sup>2</sup> and other methods. In this work, these methods were applied to the synthesis of cellulosic graft copolymers. Further, grafting of cyclic compounds catalyzed by TBAF was tried. Esterification of cellulose was carried out in TBAF / dimethyl sulfoxide (DMSO) solution recently<sup>3</sup>.

### Experimental

Celluloses used in this work were regenerated cellulose (Cell) prepared by saponification of cellulose acetate (CAc, DP 185) and cellulose powder (Avicel, DP 100~300).

Graft polymerization of celluloses was carried out as follows.

(1) ATRP method: Chloroacetylated celluloses prepared using chloro-carboxylic acid and acetic anhydride were used as an initiator in this polymerization. Styrene and methyl methacrylate (MMA) were polymerized in glyme in the presence of chloroacetylated cellulose,

copper bromide and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) at 80~130°C for 4 h. (2) MAI method: Cellulosic azo-initiators (CAI) were prepared by the reaction of Cell and CAc with 4,4'-azobis(4-cyanopentanoyl chloride) (ACPC). Vinyl monomers such as styrene and MMA were polymerized by CAI at 70°C for 4 h. (3) TBAF-catalyzed polymerization method: Avicel was dissolved in 15% TBAF/ DMSO solution at room temperature. Cyclic compounds such as lactones and N-carboxy  $\alpha$ -amino acid anhydrides (NCAs) were polymerized in this solution at 30~60°C for 4 h.

### Results

#### I. ATRP method

ATRP of styrene and MMA was carried out with chloroacetyl (ClAc) and 2-chloropropionyl (CP) cellulose.

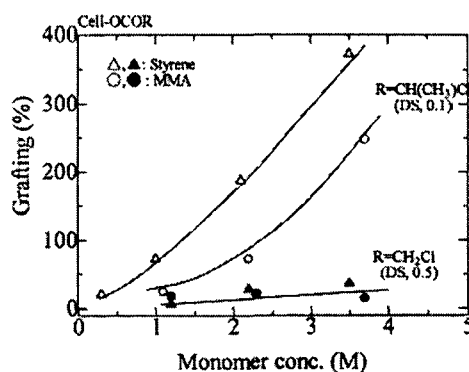
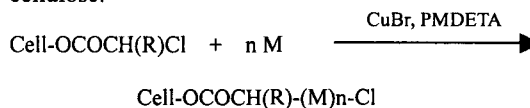
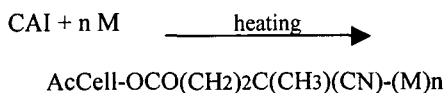
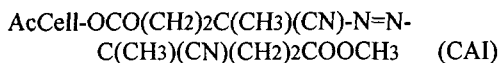


Fig. 1. Effect of monomer concentration on ATRP of styrene (triangle) and MMA (circle) initiated by chloroacetylated cellulose in glyme. Open mark: CP (DS,0.1) ; Full mark: ClAc (DS, 0.5). As shown in Fig.1, the reactivity of CP group (R=CH<sub>3</sub>) was larger than that of ClAc group

(R=H) in spite of lower degree of substitution. It was apparent that the structure of graft cellulose differed with the kind of monomers by the measurement of the molecular weight of branch polymers.

## II. MAI method

Vinyl monomers such as styrene and MMA were also easily polymerized by CAI prepared by the reaction of CAC with ACPC.



As shown in Table 1, the structure of graft cellulose differed with the kind of monomers as well as ATRP method.

**Table 1** Molecular weight of branch polymer and apparent initiator efficiency (AIE) of azo group of CAI

Monomer	DS	G (%)	MW	AIE (%)
ST	0.1	27	38000	1.9
	0.34	44	42000	0.7
	0.45	80	34000	1.3
MMA	0.08	89	235000	1.2
	0.1	177	360000	1.3
	0.34	214	215000	0.7
	0.45	228	90000	1.4

## III. TBAF-catalyzed polymerization method

It was apparent that cellulose was able to dissolve in TBAF / DMSO solution without any pre-treatment in a short time<sup>3</sup>. Table 2 shows the solubility of Avicel in this solution and tetraethylammonium chloride (TEAC) / DMSO solution.

**Table 2** Solubility of Avicel in tetraalkylammonium salt / DMSO solution

Salt	Conc. of salt (%)	Conc. of Cellulose (g/L)	Temp (°C)	Solubility
TBAF	5	20	r.t.	△
	10	20		○
	15	30		○
TEAC	20	20	90	×
	25	20		○

solubility: ○, soluble; △, viscous solution; ×, insoluble

TBAF also catalyzed the polymerization of cyclic compounds such as  $\epsilon$ -caprolactone ( $\epsilon$ -CL).

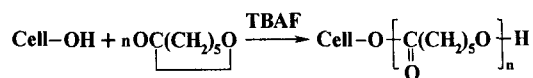
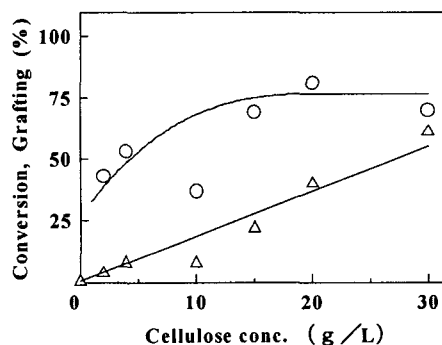


Fig.2 shows the effect of cellulose concentration on the polymerization of  $\epsilon$ -CL. Conversion increased with increase in cellulose concentration though grafting leveled off at concentrations over 15 g/L. Degree of polymerization of non-grafted poly( $\epsilon$ -CL) was below 20.



**Fig. 2.** Effect of cellulose concentration on the polymerization of  $\epsilon$ -CL.

△, conversion; ○, grafting

L-lactide was also polymerized by TBAF to form the corresponding graft cellulose.

Cellulose-g-polypeptide was synthesized by the polymerization of NCAs.

## Conclusions

Cellulosic graft copolymers were synthesized by three methods including ATRP, MAI, and TBAF-catalyzed polymerization method. Their molecular structures were different with the synthetic method. Elucidation of the relationship between the structure and functionality of graft celluloses will be a subject matter in the future.

## References

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2. A. Ueda, *Kobunshi Kako*, **44**, 73(1995).
3. T. Heinze, et al., *Macromol. Chem. Phys.*, **201** 627(2000).