

# Preparation of Bio-Based Polymers for Materials Applications

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## ABSTRACT

A new technology developed by us for the synthesis of well defined, tailored cellulose-synthetic polymer graft polymers and crosslinked cellulose graft polymers with control over the molecular weight of the synthetic polymer graft, a high degree of graft substitution, and knowledge of the backbone-graft linkage is reviewed. The potential of bio-based polymers using these new tailored cellulosic graft polymers for use in plastics, resins, and composite applications is discussed. The new graft polymers can function as compatibilizers/interfacial agents in the preparation of biopolymer-synthetic polymer composites and blends with the desirable properties of the constituent polymers incorporated into the new material system.

**Index Entries:** Bio-based polymers; cellulose-polystyrene; graft copolymer; crosslinked cellulose graft polymers; materials applications; wood-plastic composites; interfacial agents.

## INTRODUCTION

There is an increased use of petroleum oil and natural gas for the production of synthetic polymers, and, with an ever-increasing use of synthetic polymers in materials applications, this usage of petroleum oil and natural gas is dramatically increasing. The world's oil supply cannot last forever, and dire predictions are made of an energy scarcity as early as 1990.

Even more frightening is the prospect that the major portion of the world's oil supply comes from a politically unstable region. Fifteen to twenty percent of petrochemical production will be in the hands of the 18

so-called oil-producing nations corresponding to a synthetic polymer production of about 20 million tons. In 1986, more than 37% of the petroleum consumed came from overseas, nearly half of it from the Organization of Petroleum Exporting Countries. By some estimates, if these trends continue, the nation will be importing half of its oil by 1990 and nearly two-thirds by the year 2000—most from the Middle East. Recent reports—two by petroleum-industry groups and one by the Energy Department—conclude that the nation is becoming increasingly hooked on foreign oil and, therefore, more vulnerable to supply disruptions and price manipulation.

### ***Bio-Based Polymeric Materials***

The use of renewable natural biopolymers in part or totally for the production of polymeric materials would decrease the amounts of synthetic polymers needed and, hence, reduce the amount of petroleum oil needed. This could free up the oil for traditional direct energy uses. In addition, the use of the renewable natural biopolymer in polymeric material applications could result in improving properties and imparting desirable traits into the material, making the use of renewable natural biopolymer important in its own right. Increasingly strident environmental concerns caused by the discarding of nondegradable plastics from petroleum-based materials could also make the use of bio-based materials a necessity.

Biomass-derived materials are being produced at substantial levels. For example, in 1983 US paper and paperboard production was 67 million t, and the biomass derived textiles production at 1.2 million t. However, their use in plastics, resins, and in new material applications like composites is negligible. The production of only five of the leading thermoplastics in 1984 was over 31 billion lbs with a net value of over \$12 billion. Cellulose acetate films have been used in the field of print lamination, for display cards, journal covers, and so on, but these applications are now being lost to polypropylene, which is more dimensionally stable. In a study of composites in specialty markets (1), total consumption of filled and reinforced plastics came to 2.4 billion lbs in 1986. Of that, thermoset resin-based composites accounted for about 1.5 billion lbs (62.5%) and thermoplastic resin based composites for 900 million lbs (37.5%). Again, very small amounts, if any (as fillers), of the biomass derived natural polymers are used in these preparations.

### ***Graft Polymers and Polyblends***

The grafting and blending of synthetic polymers to natural polymers such as cellulose can lead to materials with unusual and useful properties for a variety of applications. Graft polymerization is an attractive means for modifying base polymers because grafting frequently results in the

superposition of properties relating to backbone and side chains (2). Grafting is especially useful when the backbone and side chain homopolymers are incompatible. Special properties of graft copolymers that lead to potential or actual applications are changes in permeability, solubility, and the mosaic structure of the solid state (3).

In this paper, we review a new technology developed for the preparation of cellulose–synthetic polymer graft polymers, whose properties may be tailored to specifications by controlling parameters such as the molecular weight of the grafted side chains, the number of grafted side chains, and the nature of the cellulose backbone–graft linkage. Cross-linked cellulosic graft polymers with complete control over the length of crosslink, nature of the crosslink, and degree of crosslinking has also been successfully prepared. With the successful synthesis of these well defined, tailored graft polymers, bio-based polymers can now potentially be used in plastics and resin applications, currently dominated by the synthetic polymers.

The new graft polymers can function as compatibilizers or interfacial agents in the preparation of biopolymer–synthetic polymer composites and blends with the desirable properties of the constituent polymers incorporated into the new material system. Indeed, the concept of appropriately combining two dissimilar polymers to form a new material system with superior properties using block or graft copolymers as compatibilizers or interfacial agents is widely practiced in the polymer industry (4–7). However, this approach has not been employed in blending biopolymers with synthetic polymers to produce new plastic materials. This is probably because well characterized cellulose block or graft polymers of defined graft molecular weight, high degree of graft substitution, knowledge of the backbone–graft linkage has not been realized with radical polymerization methods generally used for their synthesis. In this paper we will also review some of our work in the use of our new graft polymers to prepare a wood-plastic composite material system.

## BACKGROUND

The unique and interesting properties of graft polymers arise from their semimicroscopic heterogeneity. Each block retains all the characteristics of its respective homopolymer. Because the individual components are usually incompatible, the blocks of the graft copolymers try to avoid each other, creating well-defined domains of each individual homopolymer within the graft copolymer. It is this heterogeneity of the graft copolymers that allows the individual components of the graft copolymer to retain their basic properties. For example, the grafting of 8–12% of polyacrylic acid onto high density polyethylene left the melting point and crystallinity of the polyethylene backbone essentially unchanged, while imparting to it increased modulus and softening point. The water absorption and permeability were markedly increased by the grafting

(8,9). The grafting reaction can thus be seen as perhaps the only method by which certain properties can be introduced permanently into a polymer without changing its chief performance characteristics. Therefore, it is possible to impart desirable properties to the cellulosic derivative without changing its main properties by grafting a synthetic polymer with the desired property onto the cellulosic derivative.

The properties of cellulose grafts depend on the location of the grafted side chains (10). Properties such as abrasion resistance, enhanced adhesion, and wetting only need surface modification of the base polymer. Flame retardancy and water sorbency need bulk grafting. Other properties, including ion exchange ability, dimensional stability, and electrical properties can also be imparted to cellulose. The presence of cellulose has also been shown to impart biodegradability to cellulose-synthetic graft materials.

### ***Applications***

Many applications have been proposed for cellulose-synthetic polymer graft polymers. The polystyrene grafts can impart improved mechanical strengths to cellulose acetate membranes that enjoy such specialized uses as kidney dialysis, desalination of seawater, battery separators, and purification of industrial wastes. Cellulose acetate films have long been used in the field of print lamination, for display cards, journal covers, and so on, but some of the applications are now being lost to polypropylene, which is more dimensionally stable. The grafting of polystyrene or another inexpensive synthetic polymer onto the cellulose acetate would overcome the problem of dimensional stability. The low water vapor resistance and the poor performance in repeated flexing preclude cellulose acetate from most of the protective wrapping applications in packaging. Again, the performance characteristic of cellulose acetate can be improved by grafting. Indeed, the graft polymerization approach has the potential to allow greater usage and applicability for cellulose and other renewable inexpensive biopolymers in plastic films and packaging applications currently dominated by polyethylene, polystyrene, and, to a lesser extent, polypropylene.

Other potential applications can be in auto parts, indoor panels, bucket seat backs, and electrical appliances. Biodegradable bio-based materials for agricultural mulch films, housewares like plastic cups and plates, and controlled release applications for biomedical and fertilizer use are exciting new applications. Environmental concerns caused by the discarding of nonbiodegradable plastics from petroleum-based materials can be mitigated by the use of the new biodegradable plastic.

### ***Problems in Graft Polymer Preparation***

In general, changes brought about by current grafting approaches have been very modest. Much work has been done studying the grafting

of synthetic polymers to cellulosic backbones, and several extensive reviews have been written on this subject (11–15). However, almost all of the grafting methods involve radical polymerization approaches. This approach has several major disadvantages that have precluded any dramatic changes being seen in the graft polymer. They are

1. The molecular weight of the grafts is difficult to control or change.
2. The molecular weight is often very high and the molecular weight distribution wide.
3. Grafting of only a few high molecular weight grafts occurs.
4. Considerable amounts of homopolymer are sometimes formed, some of which may get embedded in the cellulose matrix and are difficult to remove.
5. No knowledge exists of the nature of the linkage between the cellulose backbone and the graft, nor the ability to control it.

In view of this lack of control over the grafting process, the tremendous applications potential of the cellulose graft polymers has never been realized.

## NEW SYNTHETIC ROUTE TO CELLULOSIC GRAFT POLYMERS

It is clear that if the tremendous applications potential of the cellulosic graft copolymers is to be realized, new synthetic approaches are needed. The new synthetic approaches should be such as to allow tailoring the properties of the graft polymers by controlling parameters such as the molecular weight of the side chain grafts, elimination or minimization of concurrent homopolymer formation, the number and type of grafted side chains, knowledge of the linkage between the cellulose backbone, and the side chain graft and the ability to control it.

We have developed new synthetic approaches to cellulosic graft polymers using anionic polymerization techniques that allow us to do this (16–19). The method involves

1. Introduction of *electrophilic or leaving groups* onto the cellulose backbone by chemical modification, i.e., introduction of reactive sites onto the cellulose backbone.
2. Preparation of the “living” synthetic polymer of desired molecular weight by anionic polymerization techniques.
3. Reaction of the “living” synthetic polymer with the modified cellulose under homogeneous reaction conditions.

Anionic polymerization methods provide an extensive and unprecedented control over polymerization processes. This includes polymer composition, microstructure, *molecular weight* and *molecular weight distri-*

bution, and monomer sequence distribution. This is the key to our approach, because we now have the ability to control the essential parameters of the side chain synthetic graft that dictates the properties of the graft polymer. By regulating the ratio between the reactive sites on the cellulose backbone and the synthetic polymer anion (the "living" synthetic polymer) one can control the degree of substitution (DS) of the graft. The synthetic polymer anion we have used is generally a carbanion (18,19) or a carboxylate (20) anion, and the reactive sites on the cellulose backbone are good leaving groups like tosylate (18,19) and mesylate (20) groups. Thus, the reaction chemistry essentially involves a  $\text{S}_{\text{N}}2$  type nucleophilic displacement reaction of the tosylate or mesylate group by the synthetic polymer anion. Therefore, there is no uncertainty in the nature of the backbone-graft linkage in our synthetic approach. Homopolymer formation is minimized and, if formed, is easily extractable.

### ***Synthesis of Cellulose–Polystyrene Graft Polymers (cell-g-PS) (19)***

Acetone-soluble cellulose acetate (DS = 2.47, DP = 110) was modified by tosylation (21) to provide good leaving group, and capping of the free hydroxyl groups on the cellulose backbone, to eliminate any possibility of homopolymer formation caused by quenching of the polystyryl carbanions by the hydroxyl protons (1, Fig. 1).

"Living" polystyrene of desired molecular weight was prepared by anionic polymerization and the resultant carbanion 2 (Fig. 1) was end capped with 1,1-diphenylethylene, to form the modified carbanion 3 so as to reduce the basicity of the polystyryl carbanion 2. This was necessitated because the strongly basic polystyryl carbanion cleaved the glycosidic bond, resulting in cellulose chain degradation and polystyrene homopolymer formation.

Reaction of the modified polystyryl carbanion 3 with the tosylated cellulose acetate 1 gave good yields of the graft polymer 4. Table 1 summarizes the amount of polystyrene grafted and the number of anhydroglucose units per grafted side chain (or number of PS chains per cellulosic chain) for three different molecular weight polystyrenes.

Proof of grafting was obtained by IR spectroscopy (Fig. 2), solubility, elemental analysis, and thin layer chromatography. Mild hydrolysis of the graft polymer 4 with aqueous ammonia resulted in removal of unreacted tosyl and acetate groups on the backbone with the formation of a cellulose–polystyrene graft polymer 5. IR spectrum of the product (Fig. 2) confirmed the structure, showing that the polystyryl chain was grafted onto the cellulose backbone via a carbon–carbon linkage and there were no acetate groups (disappearance of the carbonyl band) remaining.

Thus, cellulose–polystyrene graft polymers can be prepared in which we have control over molecular weight of the graft, and obtain a

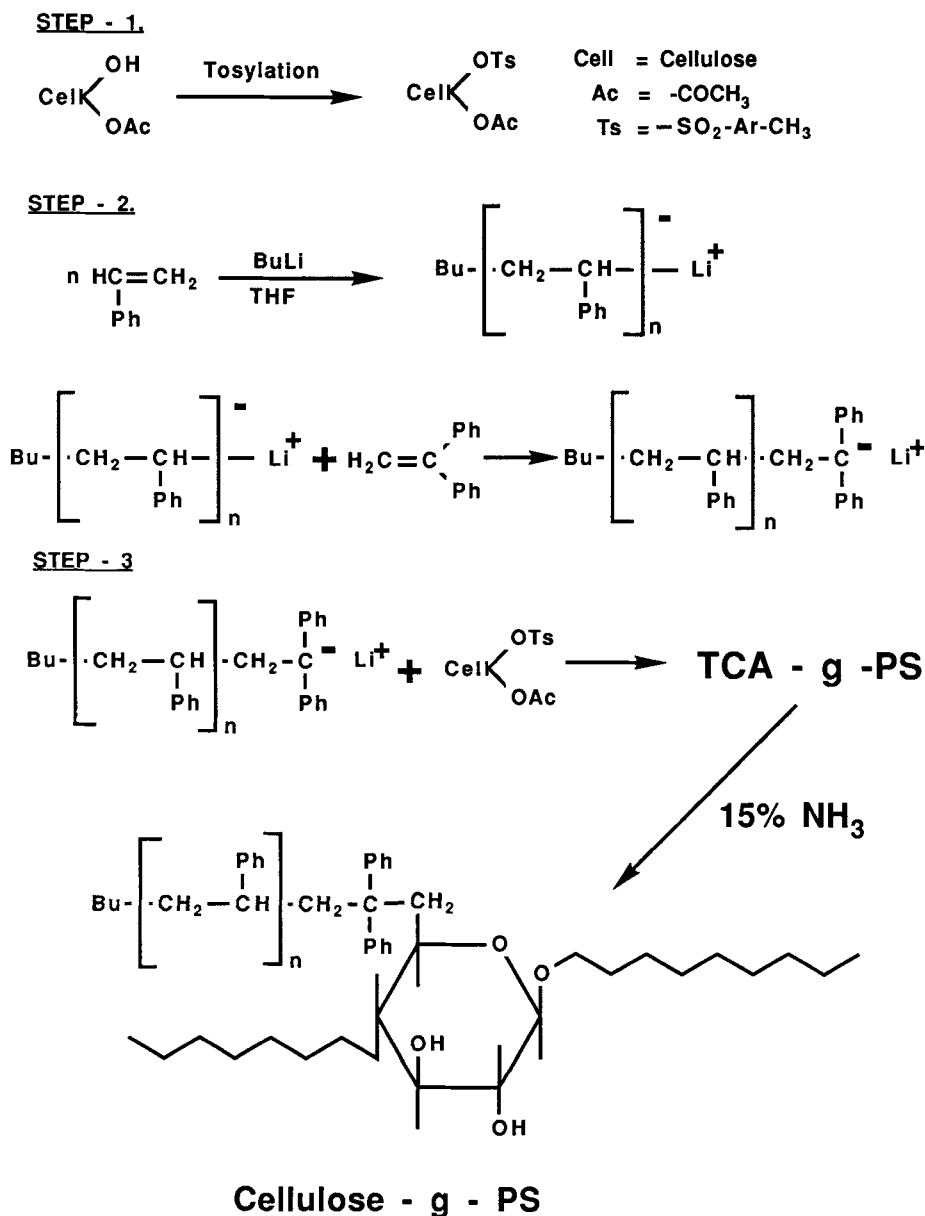


Fig. 1. Grafting of polystyrene onto tosylated cellulose acetate.

high degree of graft substitution, a carbon-carbon backbone-graft linkage. The cellulose acetate-polystyrene graft polymer is soluble in organic solvents and can be readily processed similar to conventional plastic processing. If necessary, the processed product can be subjected to mild hydrolysis to leave behind a strong, insoluble cellulose-plastic product.

We have also reported the synthesis of cellulose-polyacrylonitrile graft polymers using our anionic polymerization approach (17).

Table 1  
Results of Grafting Polystyrene onto Tosylated Cellulose Acetate

Sample no.	Molecular weight of PS	% PS, by wt	Anhydroglucose units/grafted side chain	PS chains/cellulosic chain <sup>a</sup>
1	3,400	39	16	6.7
2	10,000	51.8	28	3.9
3	32,200	42.2	135	.81

<sup>a</sup>DP = 110; DS of acetyl = 2.47; DS of tosyl = 0.42.

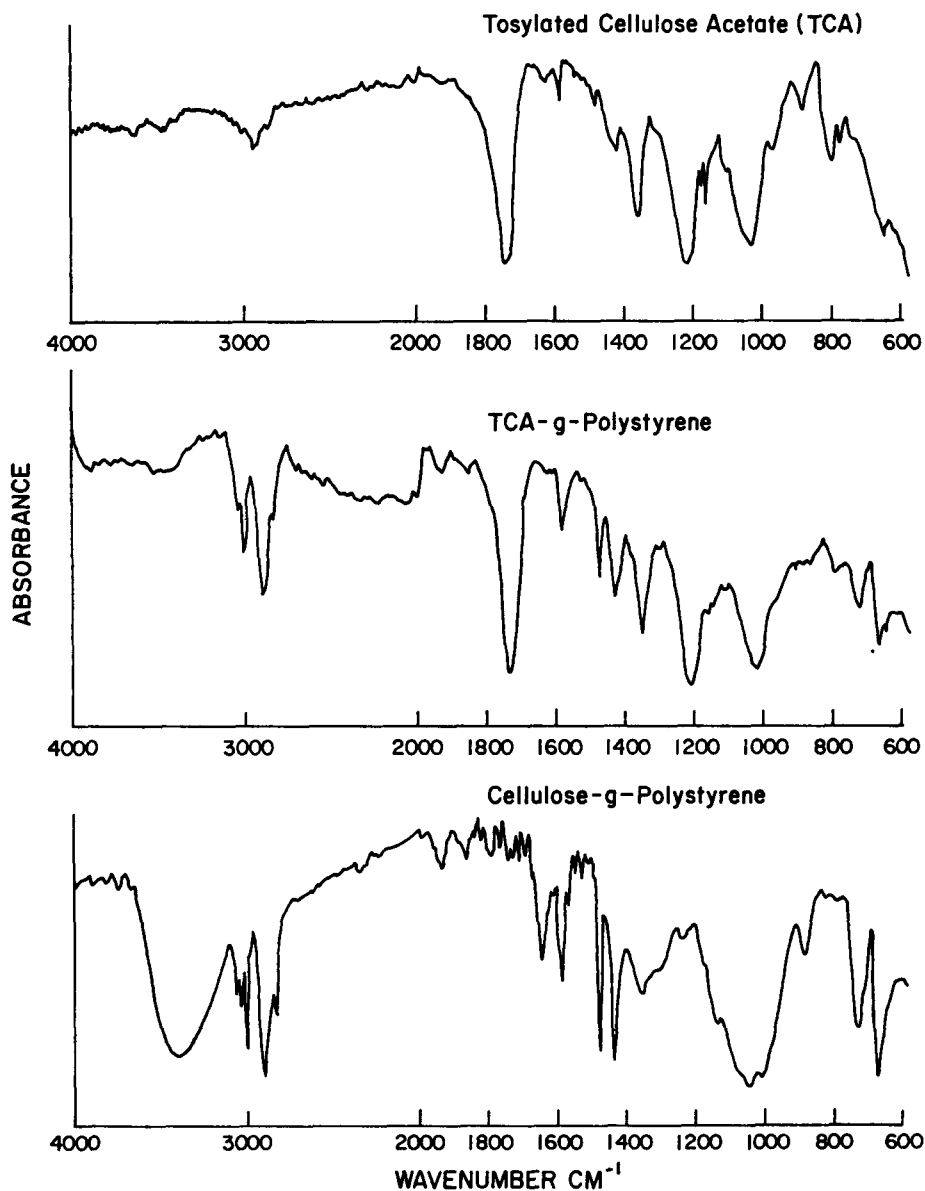


Fig. 2. IR spectra of tosylated cellulose acetate (TCA), TCA-g-polystyrene, cellulose-g-polystyrene.



### Cellulose Graft Polymers with Ester Linkages

Polysaccharide esters, like cellulose and starch esters, cannot be molded easily, if at all. For the most part, such molded products are brittle and inflexible and thus entirely unsuitable for commercial utilization. To overcome these difficulties, plasticizers are often incorporated into polysaccharide ester derivatives. Thus, relatively low molecular weight plasticizers, such as dioctyl phthalate, have been added to aid in compounding and molding as well as in modifying the properties of the finished product. This approach, however, although solving many of the original problems of brittleness and inflexibility has, in turn, raised new problems. Thus, one is faced with increased expense, poor plasticizer compatibility, and the need for new solvent systems. In addition, care must be taken in order to avoid the tendency of the plasticizer to become physically separated from the polysaccharide ester under conditions of temperature change or mechanical stress. Thus, the beneficial effect of the plasticizer may be lost by slow evaporation as well as by bleeding out of the product or upon its being leached out by solvents. It is also essential to prevent migration of the plasticizer in order to maintain the desired properties.

Extruded plastic products from cellulose acetate mixed with plasticizers are used as backing for such products as pressure-sensitive tape, goggles, and motorcycle helmet face shields. Mixed cellulose esters (cellulose acetate propionate, cellulose acetate butyrate) yield thermoplastics with properties similar to acetate but the performance level is generally better.

Using our graft polymerization synthetic scheme, we have prepared cellulose graft polymers with ester linkages with control over the molecular weight of the side chain graft (20). In this synthesis, the polystyryl carbanion, prepared by anionic polymerization techniques, has been modified by capping with carbon dioxide to generate the polystyryl carboxylate anion **1** (Fig. 3). Although this anion is not sufficiently reac-

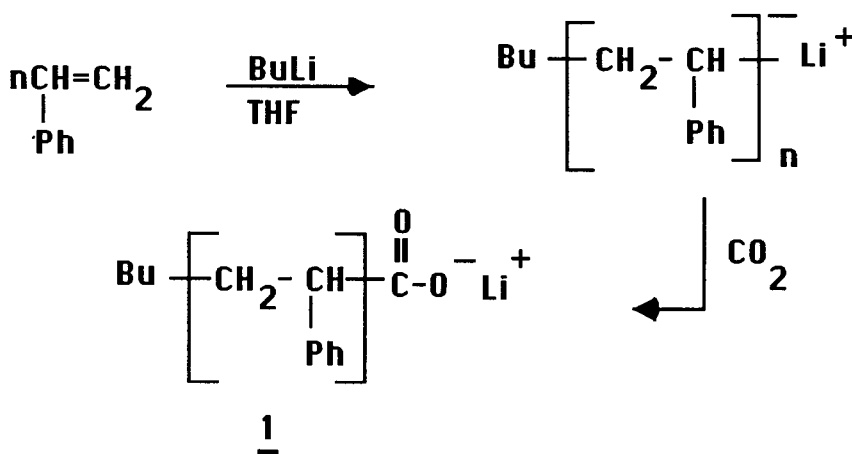


Fig. 3. Preparation of polystyryl monocarboxylate anion.

tive to displace acetate groups from cellulose acetate, it is, however, sufficiently nucleophilic to displace better leaving groups like the mesylate group from a mesylated cellulose acetate backbone with the concomitant formation of an ester linkage (Fig. 4). A further advantage of the direct use of polystyrene carboxylate anion over polystyryl carbanion is that water does not interfere with the grafting reaction. The reaction is essentially complete at 75°C after 20 h. Grafting yields appear to be limited by the efficiency of carboxylation of the polystyrene. The results are shown in Table 2. In the graft polymer product there is one polystyryl ester chain of molecular weight 6200 for every 17 anhydroglucose units of the cellulose backbone. Using this approach, monodisperse polystyryl ester chains of any predetermined molecular weight can be grafted onto the cellulose backbone in a consistent manner.

The thermoplastic grafted polymer chains of these new graft polymers can function as internal plasticizers and impart excellent molding properties. It gives a high degree of thermoplasticity as well as yields films that are tough, stable, and flexible.

### ***New Crosslinked Cellulose Graft Polymers***

Another exciting development coming out of the new grafting technology is the ability to crosslink cellulosic chains with synthetic polymers having total control over the length of the crosslink (molecular weight of the crosslinking polymer), nature of the crosslink and degree of crosslinking. Although crosslinking of cellulose, especially in the textile in-

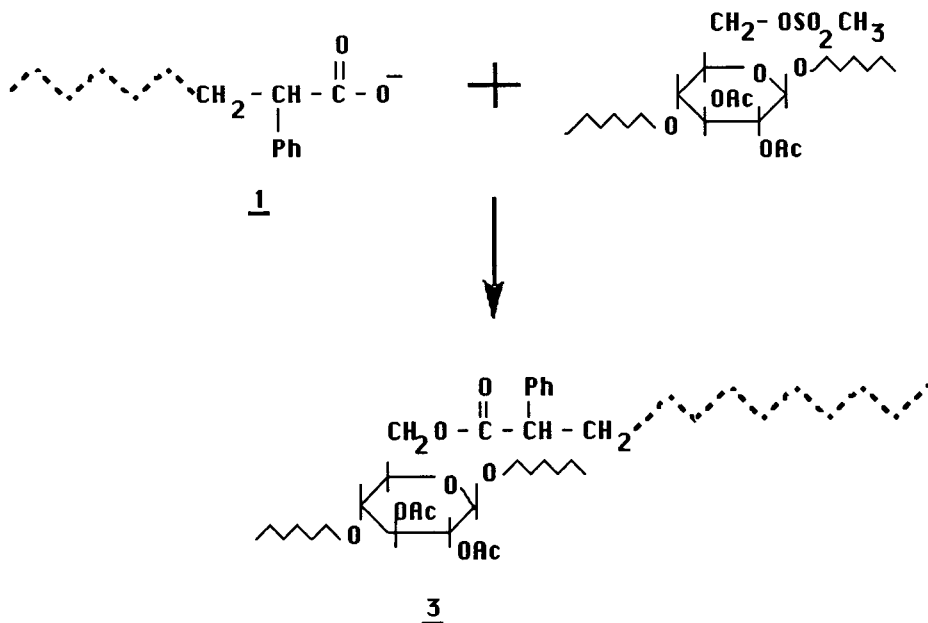


Fig. 4. Grafting of polystyryl monocarboxylate anion onto mesylated cellulose acetate.

Table 2  
Results of Grafting of Polystyrene Monocarboxylate onto Mesylated Cellulose Acetate at 75°C, 20 H

Product no.	solvent	Grafting <sup>a</sup> yield, %	PS content, <sup>b</sup> wt%	PS content	AGU <sup>d</sup> / PS chain
				by UV, wt%	
3a	DMF	68	57.6	58.2	17.0
3b	DMSO/TFT	60	54.5	59.9	19.3

<sup>a</sup>Percent by weight of the PS grafted.

<sup>b</sup>Determined from the weight increase.

<sup>c</sup>The molecular weight of the monodisperse polystyryl monocarboxylate is 6200 (Product 3).

<sup>d</sup>Number of anhydroglucose units/polystyrene side chain.

dustry, has been accomplished with monomers, there has been, to the best of our knowledge, no report of controlled crosslinking of cellulose acetate or other cellulose derivatives with synthetic polymer chains.

Anionic polymerization of styrene with sodium naphthalene as the initiator gave the difunctional polystyryl carbanion of desired molecular weight which on reaction with CO<sub>2</sub> furnished the polystyryl dicarboxylate anion (Fig. 5). Reaction of this anion with mesylated cellulose acetate resulted in the formation of a solid gel, indicative of crosslinking. Crosslinking is to be expected, since both ends of the polystyrene chain could potentially react with the mesylate groups on the cellulose backbone as shown in Fig. 6 (20). Results of the crosslinking experiment are shown in Table 3. Based on the polystyrene content of the graft polymer product and the molecular weight, there seems to be one polystyryl crosslink for every 23 anhydroglucose units.

Another new crosslinked cellulose polymer prepared in a similar manner involves the grafting of partially hydrolyzed poly(methyl methacrylate) onto mesylated cellulose acetate (23) (Fig. 7).

In the important and growing area of polymer composites, cellulosic materials have been considered only as fillers and re-enforcing materials,

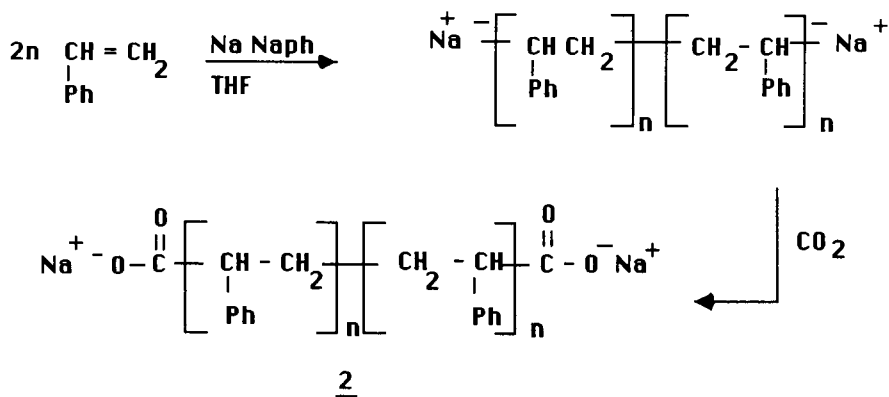


Fig. 5. Preparation of polystyryl dicarboxylate anion.

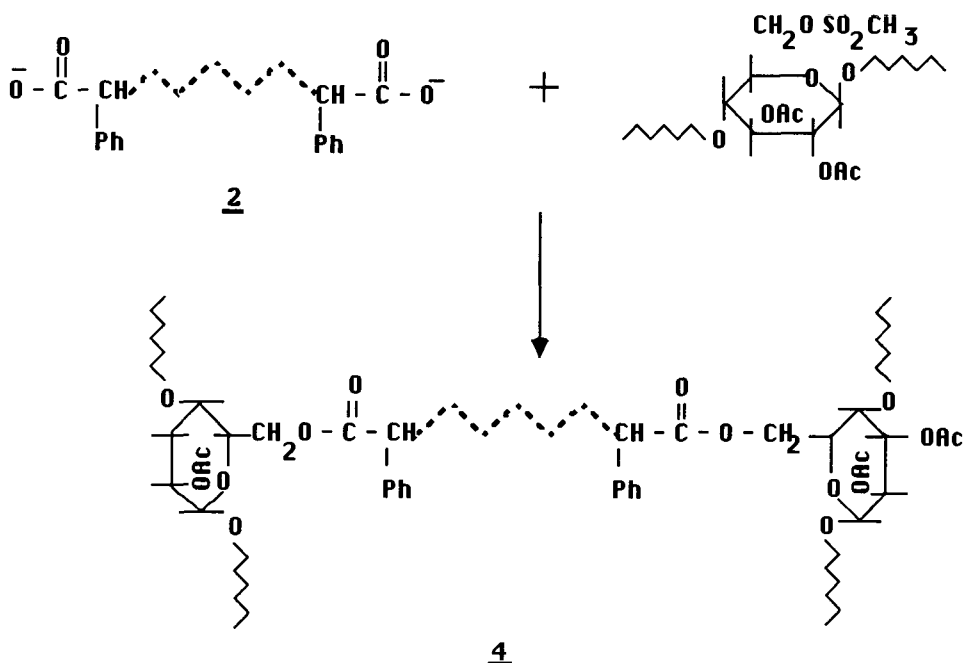


Fig. 6. Formation of a crosslinked graft polymer.

and are rarely used. The preparation of these new crosslinked cellulosic polymers offers the potential for creating a whole new set of cellulose thermoset resin-based composites.

### ***Cellulose–Polystyrene Graft Polymers as Compatibilizers or Interfacial Agents for Wood–Plastic Composites***

The preparation of new materials by mixing two incompatible polymers results in a material with properties poorer than either of the individual constituent polymers (24–26). This situation arises from a poor degree of interfacial adhesion between components because of their

Table 3  
Results of Grafting of Polystyryl Dicarboxylate Anion with Mesylated Cellulose Acetate at 75°C, 20 H

Product no.	Solvent	Grafting <sup>a</sup> yield, %	PS content, <sup>b,c</sup> wt%	AGU <sup>d</sup> /PS chain
4a	DMF	90.5	64.4	22.5
4b	DMSO/THF	88.5	63.9	23.0

<sup>a</sup>Percent by weight of the PS grafted.

<sup>b</sup>Determined from the weight increase.

<sup>c</sup>The molecular weight of the monodisperse polystyryl dicarboxylate anion is 10900 (Product 4).

<sup>d</sup>Number of anhydroglucose units/polystyrene side chain.

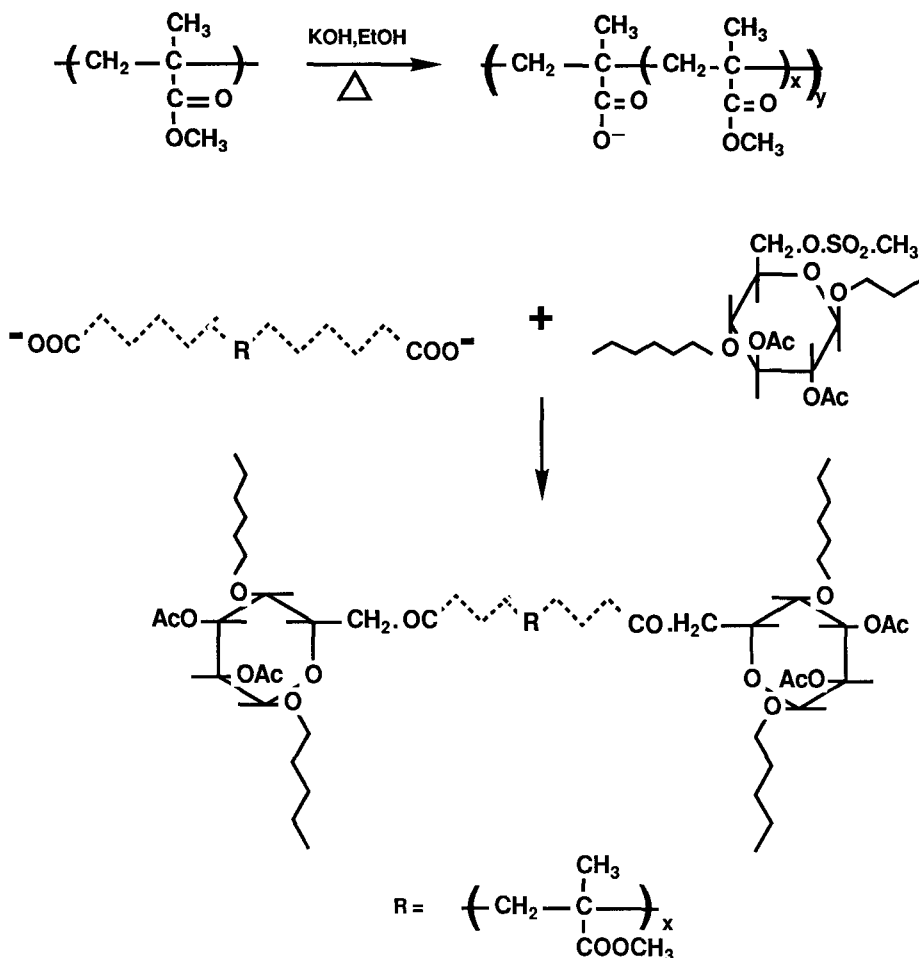


Fig. 7. Grafting reaction of partially hydrolyzed poly(methyl methacrylate) onto mesylated cellulose acetate.

inherent incompatibility. As indicated in the introduction, a solution to this compatibility problem widely practiced by the polymer industry (2–5) is the use of block or graft polymers as compatibilizers or interfacial agents to improve adhesion.

We were interested in the design and development of wood-synthetic polymer polyblends (composites) that incorporate the desirable characteristics of both polymers, leading to a new class of wood-based materials.

Again, the major problem in developing this new material system is the inherent incompatibility of the two components, the hydrophobic polystyrene and the polar wood–adhesive matrix. Thus, in order to create this new material system with improved mechanical and physical properties that incorporates the desirable features of both polymers, it is imperative to use a well-defined cellulose–polystyrene graft polymer as a

compatibilizer. The cellulose component of the wood would be bonded to the cellulose phase of the graft polymer by the resin, and the polystyrene phase of the graft polymer would melt and flow into the polystyrene component, establishing a strong bond with the polystyrene. Thus, the incompatible wood and polystyrene components will be joined via bonding through the graft polymer backbone (Fig. 8). It is also possible to extend this concept into preparing flakeboards with a continuous three-dimensional network of polystyrene bonded to the wood via the cellulose-polystyrene graft polymer. The anchoring of this polystyrene network throughout the flakeboard volume will further enhance mechanical and physical properties of the board (Fig. 9).

A set of exploratory experiments with two different cellulose-polystyrene graft polymers (cell-g-PS, as shown in Fig. 4; MW of the PS graft = 6250; PS content = 58% and cellulose-polystyrene crosslinked graft polymer as shown in Fig. 6; MW of the PS graft = 10,900; PS content = 64%) were performed to test the concept (27).

The test involved studying how the graft polymers, polystyrene, and a commercial phenolic resin interact when combined with the wood specimens. Two-ply veneer shear specimens were used in this comparative test. The specimens were fabricated and tested according to ASTM D2339-82 (28). Analysis of the test population showed that, indeed, the presence of the graft polymer had a favorable influence on the bonding of the polystyrene plastic to the wood. The average bond strength was only 334 [Standard Deviation (SD) = 181] psi, when only polystyrene and resin were present. Preliminary results using the two graft polymers increased bond strengths to 658 (SD + 228) and 819 (SD = 185) psi, respectively (27). The average bond strength of just the wood and phenolic resin was 954 (SD = 367) psi. Forty-five test specimens were used for each bond strength determination.

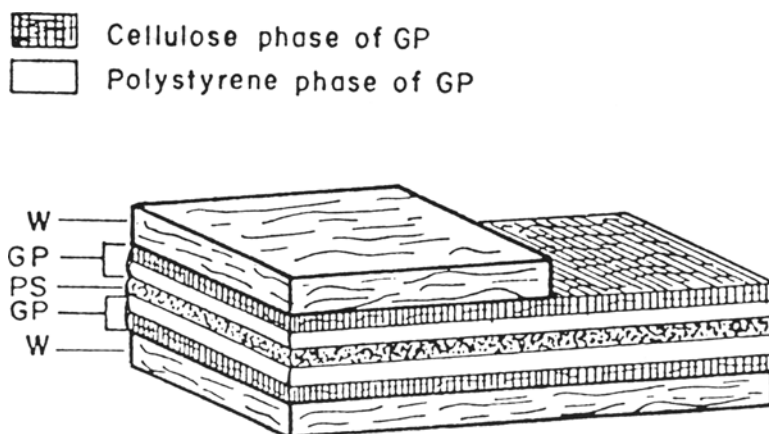


Fig. 8. Exploded view of the use of a graft polymer to compatibilize the linking of the incompatible, nonbonding wood and polystyrene (plastic) material.

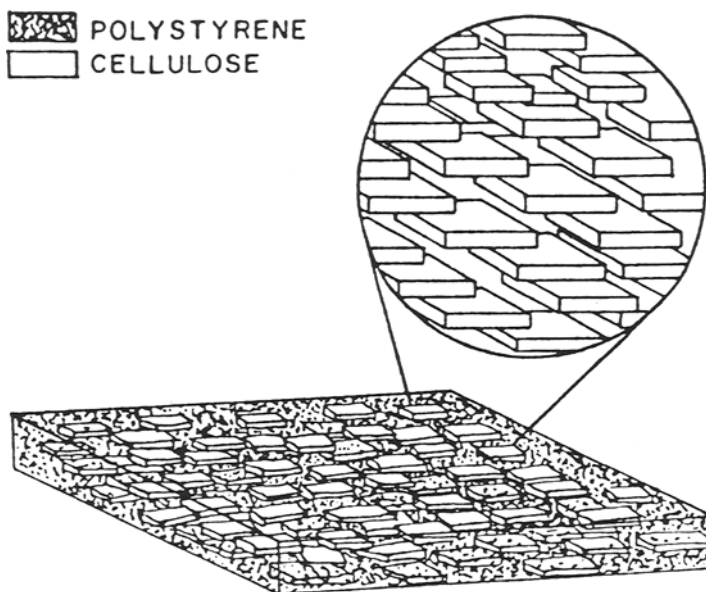


Fig. 9. A continuous three-dimensional network of polystyrene (plastic) linked to the wood via cellulose-polystyrene graft polymer.

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