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(54) Title: FREE RADICAL INITIATION SYSTEM AND METHOD OF POLYMERIZING ETHYLENICAL DICARBOXYLIC ACIDS

(57) Abstract: A polymerization initiation system comprising a free radical generator and a phosphorous-containing reducing agent is provided. This system can be used to polymerize olefinically unsaturated compounds containing at least two carboxyl groups and for forming polymers on cellulosic substrates.

FREE RADICAL INITIATION SYSTEM AND METHOD OF POLYMERIZING  
ETHYLENICAL DICARBOXYLIC ACIDS

## CROSS REFERENCE TO RELATED APPLICATIONS

This application takes priority from United States provisional patent application Serial  
5 Number 60/156,103, filed September 24, 1999, which is hereby incorporated by reference to  
the extent not inconsistent with the disclosure herein.

## BACKGROUND OF THE INVENTION

Polycarboxylic acids are useful in many fields. For example, in the fabric treatment  
field, polycarboxylic acids are promising nonformaldehyde durable press finishing agents for  
10 cotton to replace the traditional N-methylol reagents (Laemmermann, D. (1992), "New  
Possibilities for Non-Formaldehyde Finishing of Cellulosic Fibers," *Melliand Textilber.*  
**3**:274-279; Welch, C.M. (1988), "Tetracarboxylic Acids as Formaldehyde-Free Durable Press  
Finishing Agents," *Textile Res. J.* **58**:480-486; Welch, C.M. (1992), "Formaldehyde-Free  
Durable Press Finishes," *Rev. Prog. Color.* **22**:32-41; Welch, C.M. and Andres, B.A.K.  
15 (1989), "Cross-links: A Route to High Performance Nonformaldehyde Finishing of Cotton,"  
*Textile Chem. Color.* **21**(2):13; U.S. Patent 4,820,307; Yang, C.Q. et al. (1998),  
"Nonformaldehyde Durable Press Finishing of Cotton Fabrics by Combining Citric Acid with  
Polymers of Maleic Acid," *Textile Res. J.* **68**:457-464). Multifunctional acids have also been  
used as crosslinking agents to improve paper wet strength (Caulifield, D.F. (1994),  
20 "Crosslinking to Improve wet performance of Paper Using Multifunctional Carboxylic Acids,  
Butanetetracarboxylic Acid and Citric Acid," *Tappi J.* **77**(3):204-212; Horie, D. and  
Biermann, C.J. (1994), "Applications of Durable Press Treatment to Bleached Softwood  
Kraft Handsheets," *Tappi J.* **77**(8):135-140; Yang, C.Q. and Xu, Y. (1998), "Paper Wet  
Performance and Ester Crosslinking of Wood Pulp Cellulose by the Polycarboxylic Acids," *J.*  
25 *Appl. Polym. Sci.* **67**:649-658; Zhou, Y.J. et al. (1993), "Reinforcing of Paper and Board by  
Novel Crosslinking Chemicals," *Prod. Papermaking* **2**:1045-1072).

Maleic acid (MA), fumaric acid (FA), itaconic acid (IA) and other olefinically unsaturated compounds containing at least two carbonyl groups are historically extremely difficult to homopolymerize in their acidic forms in comparison to monosubstituted ethylenical acid monomers such as acrylic acid.

5 Poly(maleic acid) (PMA) has been prepared using a two-step process: polymerizing maleic anhydride (MAN) to form poly(maleic anhydride) (PMAN) in toluene in the presence of benzoyl peroxide, followed by hydrolysis of PMAN to form PMA (Culbertson, B. (1987), "Maleic and Fumaric Polymers," in Encyclopedia of Polymer Science and Technology, Kroschwitz, J.E. (ed.), Wiley, New York, pp. 231-234; French Patent No. 1,544,728; U.S. Patent No. 3,810, 834).

MA was reported to form a polymer complex with polyvinylpyrrolidone in water using potassium persulfate (Sato, T. et al. (1979), "Radical Polymerization of Maleic Acid by Potassium Persulfate in the Presence of Polyvinylpyrrolidone in Water," J. Macromol. Sci. Chem. **A13**(6):751-766).

15 Polymaleate was reported to be prepared using monosodium, monopotassium or monoammonium malate in aqueous solutions in the presence of sodium hydroxide, potassium hydroxide or ammonia and certain initiators under specialized conditions (U.S. Patent 4,668,735; U.S. Patent No. 4,709,091), or using a catalyst such as hydrogen peroxide and a vanadium, iron or copper ion (U.S. Patent No. 5,064,563) or a metal salt such as iron sulfate  
20 heptahydrate as a "promoter" in combination with a water soluble initiator (U.S. Patent No. 5,451,644).

No methods for the polymerization of FA have been found.

25 IA is easier to polymerize than MA and FA because of the 1,1-disubstitution structure of IA rather than the 1,2-disubstitution structure of MA and FA. Homopolymerization of IA was reported in 1959. This polymerization was carried out in a 0.5 N hydrochloric acid

solution with  $K_2S_2O_8$  as an initiator and took several days to complete. The conversion of IA to poly(itaconic acid) (PIA) was reported to be only 35% (Marvel, C.S. and Shepherd, T.H. (1959), "Polymerization Reaction of Itaconic Acid and Some of Its Derivatives," J. Org. Chem. **24**:599-605). IA was also reported to be polymerized in selected solvents under high  
5 pressure (5000Kg/cm<sup>2</sup>). PIA was reported to be synthesized in methanol at room temperature with AIBN as a free-radical initiator, but the polymerization took 30 days to complete with a 70% yield (Vellckovic, J. et al. (1994), "The Synthesis and Characterization of Poly(Itaconic acid)," Polym. Bull. **32**:169-170). PIA has been reported to be made in water in the presence of ferric ammonium sulfate, hydrogen peroxide and NaOH (U.S. Patent No. 5,336,744).

10 There is a need for a polymerization method for olefinically unsaturated compounds containing at least two carboxyl groups, such as maleic acid, fumaric acid and itaconic acid.

#### SUMMARY OF THE INVENTION

A polymerization initiation system comprising a free radical generator and a phosphorous-containing reducing agent is provided. The free radical generator is present at a  
15 concentration of between about 1 to about 4% of the total weight of the system, including between about 2 to about 4% of the total weight of the system, between about 1 to about 3% of the total weight of the system, and between about 2 to about 3.5% of the total weight of the system. The reducing agent is present at a concentration of between about 1 to about 25% of the total weight of the system, including between about 1 to about 10% of the total weight of  
20 the system, between about 1 to about 15% of the total weight of the system, and between about 1 to about 5% of the total weight of the system. The ranges given for the free radical generator and reducing agent include all intermediate ranges other than those specifically described herein. The mole ratio of the free radical generator:reducing agent is between about 0.1:10 to about 10:0.1, including all intermediate ranges therein, preferably between  
25 about 0.1:1 to about 1:1. An aqueous solvent is preferred, with water being most preferred. The system can also be used in an emulsion. This polymerization system can be used to polymerize olefinically unsaturated compounds with at least two carboxyl groups. The polymerization system may be used to polymerize other vinyl monomers, as well.

Homopolymers and copolymers may be prepared using the method provided herein. The system may also include an emulsifier at a concentration of between about 0.05 to about 0.5% of the total weight of the system, including all intermediate ranges therein. This method can be used to form polymers and copolymers on cellulose substrates, such as fabrics and nonwovens.

A preferred embodiment of the system is a method of polymerizing at least one olefinically unsaturated compound containing at least two carboxyl groups, such as maleic acid (cis-1,2-ethylenedicarboxylic acid, MA), fumaric acid (trans-1,2-ethylenedicarboxylic acid, FA), itaconic acid (1,2-propene-3-dicarboxylic acid, IA), citraconic acid, cis-aconitic acid, trans-aconitic acid and 3-butene-1,2,3-tricarboxylic acid, which comprises: (a) mixing a phosphorous-containing reducing agent, one or more olefinically unsaturated monomers which contain at least two carboxyl groups, and a free radical generator to form a mixture; and (b) subjecting said mixture to polymerization conditions. The monomer or mixture of monomers may be present in the mixture at a concentration of between about 1 and about 50% of the total weight of the mixture and all intermediate ranges therein, including between about 1 to about 25% of the total weight of the mixture, between about 10-40% of the total weight of the mixture and between about 25-50% of the total weight of the mixture. The reducing agent may be present in the mixture at a concentration of between about 1 and about 25% of the total weight of the mixture and all intermediate ranges therein, preferably between about 1 and about 15% of the total weight of the mixture and those ranges specifically listed above. The mole ratio of the free radical generator:reducing agent is between about 0.1:10 to about 10:0.1 and all intermediate ranges therein. It is preferred that the mole ratio of the free radical generator:reducing agent be between about 0.1:1 to about 1:1.

Another preferred embodiment of the polymerization system is a method of forming polymers on cellulose substrates, such as fabrics and nonwovens comprising: (a) immersing a substrate in a solution comprising at least one monomer that contains at least two carboxyl groups at a monomer concentration of between about 2 and about 15 % of the total weight of solution, said solution also comprising a free radical generator at a concentration of between

about 1 and about 4 % of the total weight of solution and a phosphorous-containing reducing agent at a concentration of between about 1 and about 10 % of the total weight of solution; and (b) curing the substrate. Polymers and copolymers may be produced in-situ on cellulose substrates, including fabrics and nonwovens, preferably cotton fabric, by this method.

5 Polymers and copolymers may be produced on other fabrics as well, such as rayon and cotton-polyester blends. Preferred copolymers include MA and IA. The preferred ratio of MA to IA is between about 1:1 to about 4:1. All ranges given for the monomers, free radical generators and reducing agents and other components include all intermediate ranges therein, including those specifically listed herein. It is preferred that the free radical generator be  
10 present at a concentration of about 2% of the total weight of solution. It is preferred that the reducing agent be present at a concentration of about 4% of the total weight of solution. The system may also include an emulsifier at a concentration of between about 0.05 to about 0.5% of the total weight of the system.

Also provided is a polymerization system comprising: a free radical generator at a  
15 concentration of between about 1 to about 4% of the total weight of the system and a phosphorous-containing reducing agent at a concentration of between about 1 to about 25% of the total weight of the system and an aqueous solvent. The free radical generator is preferably selected from the group consisting of:  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  at a concentration of above about 2% of the total weight of the system. The reducing agent is  
20 preferably selected from the group consisting of:  $\text{NaH}_2\text{PO}_2$  and  $\text{Na}_2\text{HPO}_3$  at a concentration of between about 1 to 10% of the total weight of the system. The mole ratio of said free radical generator:phosphorous-containing reducing agent is preferably between about 0.1:10 to about 10:0.1. This system may further comprise one or more olefinically unsaturated compounds containing at least two carboxyl groups at a concentration of between about 1 to about 50% of  
25 the total weight of the system, and all intermediate ranges therein, including those specifically listed herein.

"Curing" the substrate involves subjecting the substrate to a temperature of between about 150 and about 200°C, as known in the art. Preferably a temperature of about 180°C is

used to cure the substrate. The substrate may be dried after immersion in the polymerization solution and before curing. Drying may occur at any suitable temperature, preferably about 70 to 100°C, as is known in the art.

5 Substrates include cellulose substrates such as fabric and nonwovens. Cotton fabric is a preferred substrate.

10 The polymerization method for ethylenical dicarboxylic acids such as MA, FA and IA described uses those acids in their acidic forms and the temperature range normally used for aqueous free radical polymerization (about 60-100°C) without any "promoters" other than the reduction-oxidation initiation system itself. It can achieve >95% monomer conversion within a relatively short period of time (for example, about 1 hr). PMA synthesized with this method has significantly lower monomer content than the commercially available PMA, which is produced by polymerizing MAN followed by alkaline hydrolysis of PMAN.

15 As used herein, "free radical generator" takes its usual meaning in the art and is also referred to as an initiator. Examples of preferred free radical generators include salts of persulfates such as  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and water soluble peroxides such as hydrogen peroxide. Free radical generators used herein are water soluble.

As used herein, reducing agent takes its usual meaning in the art and includes those substances that donate electrons to another species. Reducing agents useful in the invention are those that contain phosphorous, including, but not limited to  $\text{NaH}_2\text{PO}_2$  and  $\text{Na}_2\text{HPO}_3$ .

20 As used herein, polymerization conditions include those under which polymerization can occur. Polymerization conditions include a temperature of between about 40 and about 100 °C and all intermediate ranges therein, including from about 40 to about 80 °C and from between about 50 to about 85 °C. The polymerization typically takes between about five minutes to about six hours to produce the desired degree of polymerization. Preferred  
25 polymerization conditions include a temperature of between about 60 to about 100 °C and a

time of between about thirty minutes to about four hours. One of ordinary skill in the art can determine suitable polymerization conditions without undue experimentation using the teachings described herein and the teachings known in the art.

As used herein, "mixing" reaction components with each other refers to providing a medium and/or reaction chamber in which the reaction components are placed together so that they can react with each other. Preferably, the reaction components are suspended or dissolved in a solvent which is a liquid medium. More preferably, an aqueous solution is used as the solvent. Most preferably, water is used as the solvent. Alternatively, an emulsion may be used where an emulsifier such as sodium dodecyl sulfate is used and insoluble monomers such as esters of maleic acid, fumaric acid or itaconic acid are polymerized. In the case of using emulsions, a mixture of water, emulsifier, monomer, free radical generator and reducing agent is used. When emulsions are used, the concentration of components can be higher than when components are dissolved in a solvent.

A "mixture" of compounds is not meant to imply that the compounds necessarily form a completely soluble solution. Mixture merely means that the compounds contact each other. The compounds forming the mixture may be completely or partially soluble in the solvent or may form an emulsion.

Olefinically unsaturated compounds which contain at least two carboxyl groups include those compounds where the carbon-carbon double bond is a terminal group of the compound, such as IA and those compounds where the carbon-carbon double bond is positioned within the carbon chain of the backbone, such as MA and FA. The methods of the invention are useful to polymerize ethylenical dicarboxylic acids other than those specifically illustrated. Olefinically unsaturated compounds which contain at least two carboxyl groups are also referred to as ethylenical dicarboxylic acids. The olefinically unsaturated compounds useful in the invention may contain more than one double bond. In addition, olefinically unsaturated compounds which contain only one carboxyl group may be polymerized using the method of the invention. Copolymers may be prepared using the method of the invention



using one or more olefinically unsaturated compounds which contain at least two carboxyl group and one or more olefinically unsaturated compounds which contain only one carboxyl group, such as methacrylic acid.

In addition to homopolymers, copolymers are also prepared by the method of the invention. Such copolymers include, but are not limited to copolymers formed from the polymerization of MA and IA and copolymers formed from the polymerization of fumaric acid, maleic acid or itaconic acid with a second monomer. Copolymers may be formed from an ethylenical dicarboxylic acid and a vinyl monomer.

In one embodiment, one or more of the ethylenical dicarboxylic acids (e.g., MA, FA, and IA) and the reducing agent (e.g.,  $\text{NaH}_2\text{PO}_2$ ) are mixed and dissolved in water. The monomer concentration is about 1 - 50% depending on the solubility of the monomer. The concentration of the reducing agent is from about 1 to about 25%, preferably about 2 - 10%. The mixture is heated to desired temperatures ranging from about 40 - 100°C, preferably from about 60 to 100°C. The heat may be applied before, after or during the addition of the free radical generator and reducing agent. The free radical initiator (e.g.,  $\text{K}_2\text{S}_2\text{O}_8$ ) is added before the heating process or when the mixture reaches the desired temperature. The whole amount of the free radical initiator can be added at one time, or portions of the free radical initiator can be added batchwise during the polymerization process. A portion of the total amount of free radical initiator used can be added to the mixture before applying heat and a portion of the total amount of free radical initiator can be added to the mixture after applying heat. The mole ratio of the free radical initiator/monomers is from about 0.1:10 to 2:10, preferably 0.5:10 to 1:10. The mole ratio of the free radical initiator/reducing agent is from about 0.1:10 to about 10:0.1, preferably from about 0.2:1 to about 2:1.  $\text{N}_2$  may be used to purge the polymerization system. The polymerization time is typically from about 5 mins to about 6 hr, preferably from about 30 mins to about 2 hr. The polymerization process can be carried out in aqueous solutions as solution polymerization or in emulsions as emulsion polymerization. For emulsion polymerization, an emulsifier is used, and monomers, such as esters of MA, FA and IA, insoluble in water are polymerized.

The polymers of olefinically unsaturated compounds produced by this method can be used as durable press finishing agents for fabrics, scale inhibitors for water treatment, and incrustation inhibitors in detergents, among other uses.

5 Unless otherwise noted, the percentages listed are percentage of the total weight of solution.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1: Raman spectra of 6%  $K_2S_2O_8$ : (A) before heating; (B) heated at 50°C for 120 min; (C) heated at 100°C for 10 min; and (D) Raman spectrum of 6%  $K_2SO_4$  without heating.

10 Figure 2: Raman spectrum of (A) the aqueous solution of 10%  $NaH_2PO_2$ ; (B) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  at 65°C; (C) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  heated at 65°C for 10 min; and (D) the mixture of 4.7%  $NaH_2PO_2$  and 6%  $K_2S_2O_8$  heated at 65°C for 20 min.

15 Figure 3: Raman spectra of the mixture of 25% MA and 10%  $NaH_2PO_2$  (A) before heating; (B) instantly after the first ¼ of 3.1%  $K_2S_2O_8$  was added at 90°C; (C) after the second ¼ of 3.1%  $K_2S_2O_8$  was added when the mixture was kept at 90°C for 10 min; (D) after the third ¼ of 3.1%  $K_2S_2O_8$  was added when the mixture was kept at 90°C for 20 min; (E) after the fourth ¼ of 3.1%  $K_2S_2O_8$  was added when the mixture was kept at 90°C for 30 min; and (F) when the mixture was kept at 90°C for total of 75 min.

20 Figure 4: The GPC chromatograms of PMA: (A) Reflective index detector; and (B) 90° light scattering detector.

Figure 5: Cumulative weight fraction versus molar mass of PMA.

Figure 6: The Raman spectra of (A) the mixture of 0.7% FA and 10%  $\text{NaH}_2\text{PO}_2$ , (B) the mixture of 18.6% FA, 10%  $\text{NaH}_2\text{PO}_2$  and 2.5%  $\text{K}_2\text{S}_2\text{O}_8$  kept at  $95^\circ\text{C}$  for 5 min; and (C) the mixture of 18.6% FA, 10%  $\text{NaH}_2\text{PO}_2$  and 2.5%  $\text{K}_2\text{S}_2\text{O}_8$  first kept at  $95^\circ\text{C}$  for 10 min, then at  $82^\circ\text{C}$  for 30 min.

5            Figure 7: The Raman spectra of the mixture 24.3% IA and 8.6%  $\text{NaH}_2\text{PO}_2$ : (A) when the temperature was increased to  $95^\circ\text{C}$ ; (B) when the first  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added, then the mixture was kept at  $95^\circ\text{C}$  for 10 min; (C) when the second  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added and the mixture was kept at  $95^\circ\text{C}$  for another 10 min; (D) when the third  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added and the mixture was kept at  $95^\circ\text{C}$  for another 10 min; and (E) when the  
10            mixture was kept at  $95^\circ\text{C}$  for total of 60 min.

Figure 8: Infrared spectra of (A) cotton treated with 6.0% MA and dried at  $80^\circ\text{C}$ , (B) cotton thus treated and cured at  $180^\circ\text{C}$  for 2 minutes, and (C) difference spectrum, B-A.

Figure 9: Infrared spectra of (A) cotton treated with 6.7% IA and dried at  $80^\circ\text{C}$ , (B) cotton thus treated and cured at  $200^\circ\text{C}$  for 2 minutes, and (C) difference spectrum, B-A.

15            Figure 10: Infrared spectra of (A) cotton treated with 6.0% PMA and dried at  $80^\circ\text{C}$ , (B) cotton thus treated and cured at  $180^\circ\text{C}$  for 2 minutes, and (C) difference spectrum, B-A.

Figure 11: Difference spectra of cotton treated with 6.7% IA and 4.0%  $\text{NaH}_2\text{PO}_2$  in combination with different concentrations of  $\text{K}_2\text{S}_2\text{O}_8$  (0.00, 0.25, 0.50, 1.00, and 2.00%, A-E) before and after curing at  $180^\circ\text{C}$  for 2 minutes.

20            Figure 12: CIE whiteness index of cotton treated with 6.7% IA and 4%  $\text{NaH}_2\text{PO}_2$  in combination with different concentrations of  $\text{K}_2\text{S}_2\text{O}_8$  and cured at  $180^\circ\text{C}$  for 2 minutes.

Figure 13: Percentage of free monomers (w/w) of cotton treated with 6% MA, 6.7% IA, and 4%  $\text{NaH}_2\text{PO}_2$  in combination with different concentrations of  $\text{K}_2\text{S}_2\text{O}_8$  and cured at  $180^\circ\text{C}$  for 2 minutes.

Figure 14: Infrared spectra of (A) cotton treated with 6.7% IA, 4.0%  $\text{NaH}_2\text{PO}_2$ , and 2.0%  $\text{K}_2\text{S}_2\text{O}_8$ , cured at  $180^\circ\text{C}$  for 2 minutes, subjected to ten washing cycles, treated with acetic acid, (B) cotton thus treated and then cured at  $180^\circ\text{C}$  for 2 minutes, (C) difference spectrum, B-A.

## EXPERIMENTAL

Materials: MA, FA, IA,  $\text{NaH}_2\text{PO}_2$ , and  $\text{K}_2\text{S}_2\text{O}_8$  were reagent-grade chemicals supplied by Aldrich Chemical Company. The commercial product PMA was an aqueous solution with 50% solid supplied by FMC Corporation with the trade name of Belclene 200. All the percentage concentrations are based on weight (% w/w).  $\text{N}_2$  was used to purge the system during polymerization.

FT-Raman Spectroscopic Measurements: Nicolet 950 FT-Raman spectrometer with a liquid sample accessory and an InGaAs detector was used to collect all the Raman spectra. The resolution was  $8\text{ cm}^{-1}$  and there were 100 scans for each spectrum. No baseline correction or smoothing functions were used to process the data.

Matrix-assisted Laser desorption and ionization (MALDI) time-of-flight (TOF) mass spectroscopy experiments: The matrix used was 3,5-dimethoxy-4-hydroxycinnamic acid, supplied as a reagent grade chemical by Aldrich, dissolved as a saturated solution in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1:1 based on weight) in the presence of 0.1% trifluoroacetic acid.  $1\ \mu\text{l}$  of the matrix was mixed with  $1\ \mu\text{l}$  of the polymer sample and allowed to dry at room temperature. The mass spectrum was run using Bruker Reflex MALDI/TOF mass spectrometer with a delayed extraction mode. 90 Laser shots were averaged to give the mass spectrum.

A Waters GPC system consisting of 515 HPLC pump, 410 Differential Refractometer, a Rheodyne 7725i sample injector and a Ultrahydrogel 250 column in combination with a Dawn DSP MALLS photometer (Wyatt Technology, Santa Barbara, CA) was used to measure the molecular weight distribution of the polymer. The GPC data were collected and processed by ASTRA 4.70 software (Wyatt Technology). A 0.5M aqueous NaNO<sub>3</sub> solution with a flow rate of 0.8 ml/min was used as a mobile phase at room temperature. The injection volume was 20 $\mu$ l. The light scattering photometer was equipped with a laser at 633nm. It was calibrated using toluene, and the Rayleigh ratio was determined to be 1.406x10<sup>5</sup>cm<sup>-1</sup>. Normalization was carried out using a standard polyethylene oxide sample with molecular weight of 23,000. The differential refractive index increment (dn/dc) of PMA in 0.5M NaNO<sub>3</sub> was 0.144ml/g as reported in the literature (J. Groot, J.G. Hollander, J. Bleijser, *Macromolecules*, 30, 6884 (1997)).

For the cotton polymerization and crosslinking experiments, the cotton fabric was a desized and bleached plain weave 100% cotton fabric (Testfabrics Style 400). The polyethylene softener was an industrial product made by Sequa, Chester, South Carolina (Tradename Mykon HD).

For fabric treatments, a cotton fabric sample was first immersed in an aqueous solution containing the desired chemicals. The treated fabric sample was passed through a two-roll laboratory padder made by Rapid Labortex through two dips and two nips, and dried at 80°C for 3 min. The wet pick-up was in the range of 95-100%. The fabric was then cured in a Mathis curing oven at a specified temperature. All the concentrations are presented as % weight of bath (wob).

The fabric properties measured and the standard methods used are presented in Table 1. The fabric properties were evaluated after one home laundering washing/drying cycle without a detergent. The performance of the finished fabric was also evaluated after different numbers of home laundering washing/drying cycles. The home laundering washing process was conducted according to AATCC standard method 124-1992. The fabric CIE whiteness

index (WI) was measured before washing using LabScan 6000 spectrophotometer made by Hunter Associates Laboratory.

For the fabric FTIR spectroscopy measurements, all the infrared spectra were diffuse reflectance spectra collected with a Nicolet 510 FT-IR spectrometer and a Specac diffuse reflectance accessory, and were presented in the absorbance mode ( $-\log R/R_0$ ). Resolution for all the infrared spectra was  $4\text{ cm}^{-1}$ . Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. No smoothing functions or baseline correction are used.

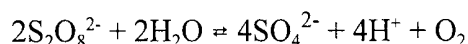
Chemical analysis: Wet analysis was used to determine the alkene double bond concentration in the treated cotton fabric. The treated fabric sample was first ground in a Wiley mill to form a powder before analysis. A NaOH solution was added to the powder to convert the unsaturated carboxylic acids to their sodium salts, followed by the addition of a saturated NaBr methanol solution with excess NaBr. Quantitative addition reaction of the unsaturated carboxylic acids by  $\text{Br}_2$  takes place when a standard  $\text{Br}_2/\text{NaBr}$  aqueous solution was added to the mixture. The quantity of the excess amount of  $\text{Br}_2$  was then determined by iodometric titration. The percentage of the remaining free monomers (e.g., MA and IA) on fabric was calculated by the quantity of  $\text{Br}_2$  consumed and the equation described as follows: [(no. of mmoles of  $\text{Br}_2$  consumed by one gram of the fabric after curing)  $\div$  (no. of mmoles of  $\text{Br}_2$  consumed by one gram of the fabric before curing)]x 100%.

TABLE 1. Standard testing methods used to evaluate fabric performance

Fabric property	Standard method
Conditional wrinkle recovery angle	AATCC 66-1990
Durable press rating	AATCC 124-1992
Tensile (breaking) strength	ASTM D5035-90
Tearing strength	ASTM D1424-83
Flex abrasion resistance	ASTM D3885-92
CIE whiteness index	AATCC 110-1995

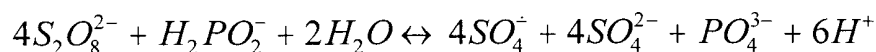
#### Decomposition of $K_2S_2O_8$ in the Presence of $NaH_2PO_2$

10 The Raman spectrum of the aqueous solution of 6%  $K_2S_2O_8$  is presented in Figure 1A, in which the bands at 1075 and 835  $cm^{-1}$  are the S=O and S-O stretching modes of  $K_2S_2O_8$ . These two bands remain unchanged when the  $K_2S_2O_8$  solution is heated at 50°C for 120 min, indicating that  $K_2S_2O_8$  does not decompose under such a condition (Figure 1B). When the  $K_2S_2O_8$  solution is heated at 100°C for 10 min, a new band at 980  $cm^{-1}$  appears in the spectrum (Figure 1C). The band at 980  $cm^{-1}$  is due to the S=O stretching mode of  $SO_4^{2-}$  as seen in the spectrum of  $K_2SO_4$  (Figure 1D). The data indicate that the thermal decomposition of  $K_2S_2O_8$  starts to take place at 100°C.



20 Shown in Figure 2A is the Raman spectrum of the aqueous solution of 10%  $NaH_2PO_2$ . The strong band at 1043  $cm^{-1}$  in Figure 2A is due to the P=O stretching mode of  $NaH_2PO_2$ . A weak band at 980  $cm^{-1}$  due to  $SO_4^{2-}$  appears in the Raman spectrum when 4.7%  $NaH_2PO_2$  is added to an aqueous solution of 6%  $K_2S_2O_8$  (Figure 2B). The bands at 980  $cm^{-1}$  due to  $SO_4^{2-}$  becomes stronger and the two bands at 1075 and 835  $cm^{-1}$  due to  $S_2O_8^{2-}$  become weaker when the aqueous solution of 6.0%  $K_2S_2O_8$  and 4.7%  $NaH_2PO_2$  is heated at 65°C for 10 min (Figure 25 2C). The data indicate that a reduction-oxidation reaction between  $K_2S_2O_8$  and  $NaH_2PO_2$

shown below takes places and the free radicals are formed as a result of the decomposition of  $S_2O_8^{2-}$ .



The two bands at 1075 and at 835  $cm^{-1}$  disappear almost completely when the solution  
 5 of 6.0%  $K_2S_2O_8$  and 4.7%  $NaH_2PO_2$  is heated at 65 °C for 20 min (Figure 2D). The band at  
 1043  $cm^{-1}$  in Figure 2D is probably overlapped by the P=O stretching mode of  $PO_4^{3-}$ , which  
 shows broadening as  $S_2O_8^{2-}$  decomposes (Figures 2B-2D). Comparison of the spectra of  
 $K_2S_2O_8$  (Figure 1) and those of the mixture of  $K_2S_2O_8$  and  $NaH_2PO_2$  (Figure 2) clearly  
 demonstrates that the temperature required for the thermal decomposition of  $K_2S_2O_8$  and the  
 10 formation of the free radical is significantly reduced in the presence of  $NaH_2PO_2$ . The  
 reduction-oxidation reaction between  $K_2S_2O_8$  and  $NaH_2PO_2$  is believed to reduce the  
 temperature at which the free radical is formed.

### Polymerization of MA

An aqueous solution of 25% MA and 10%  $NaH_2PO_2$  was prepared. The stretching  
 15 modes of the unsaturated =C-H and the alkene (C=C) of MA appear at 3060 and 1649  $cm^{-1}$ ,  
 respectively, in the Raman spectrum (Figure 3A). The strong band at 866  $cm^{-1}$  in Figure 3A is  
 due to out-of-plane deformation of the unsaturated =C-H of MA. In a MA molecule, the  
 carboxylic acid carbonyl is conjugated with C=C, thus reducing the frequency of the  
 carboxylic carbonyl stretching mode to 1707  $cm^{-1}$  (Figure 3A). A total of 3.1%  $K_2S_2O_8$  based  
 20 on the total weight of the reaction solution was added to the MA/ $NaH_2PO_2$  mixture  
 batchwise after the temperature of the mixture was increased to 90 °C. One fourth of 3.1%  
 $K_2S_2O_8$  is added instantly as the temperature reaches to 90 °C (Figure 3B), and one fourth of  
 $K_2S_2O_8$  is added after each 10 min. When the reaction mixture was kept at 90 °C for 10 min  
 and the second  $\frac{1}{4}$  of  $K_2S_2O_8$  was added, one observes that a band at 2942  $cm^{-1}$  due to the  
 25 stretching mode of saturated C-H as well as a band at 982  $cm^{-1}$  due to  $SO_4^{2-}$  emerge and the  
 bands at 1649 and 866  $cm^{-1}$  due to C=C and =C-H of MA reduce their intensity in the  
 spectrum (Figure 3C). The data indicate that polymerization of MA takes place under such a



condition. The last  $\frac{1}{4}$  of  $K_2S_2O_8$  was added when the reaction mixture was kept at  $90^\circ C$  for 30 min (Figure 3E). The band at  $3060\text{ cm}^{-1}$  due to unsaturated  $=C-H$  and the band at  $1649\text{ cm}^{-1}$  due to  $C=C$  appear to be very weak and the band at  $982\text{ cm}^{-1}$  due to  $SO_4^{2-}$  further increases its intensity (Figure 3E). When the reaction mixture was kept at  $90^\circ C$  for 75 min, the characteristic bands of MA at  $3060$ ,  $1649\text{ cm}^{-1}$  and  $866\text{ cm}^{-1}$  almost disappear completely (Figure 3F). The carboxylic acid carbonyl band shifts to  $1721\text{ cm}^{-1}$  in Figure 3F. The band at  $1387\text{ cm}^{-1}$  in Figure 3A is due to the combination of  $C-O$  stretching and  $-O-H$  deformation of the dimer of MA. As MA polymerized to become PMA, this band shifted to a higher frequency at  $1420\text{ cm}^{-1}$ , which was at the same frequency of the same band of succinic acid. The band at  $912\text{ cm}^{-1}$  in Figure 3F, which gradually increased its intensity as the polymerization processed (Figure 3C-3F), was associated with  $OH\dots O$  out of plane deformation of PMA. The assignment of the characteristic bands in the Raman spectra are summarized in Table 2. The band at  $982\text{ cm}^{-1}$  due to  $SO_4^{2-}$  increased its intensity during the gradual decomposition of  $K_2S_2O_8$  (Figures 3C-3F).

Table 2. The frequencies of the characteristic bands and their assignment in the FT-Raman spectra (Figures 1-3).

Compound	Band Frequency ( $\text{cm}^{-1}$ )	Assignment
$\text{K}_2\text{S}_2\text{O}_8$	1075	symmetric stretching mode of S=O
	835	stretching mode of S-O
$\text{K}_2\text{SO}_4$	980	stretching mode of S=O
$\text{NaH}_2\text{PO}_2$	1043	stretching mode of P-O
MA	3060	stretching mode of =C-H
	1707	stretching mode of C=O (unsaturated carboxylic acid)
	1649	stretching mode of C=C
	1387	combination of C-O stretching and -O-H deformation (dimer, unsaturated carboxylic acid)
	866	out-of-plane deformation of =C-H
PMA	2942	stretching mode of saturated C-H
	1721	stretching mode of C=O (unsaturated carboxylic acid)
	1420	combination of C-O stretching and -O-H deformation (dimer, saturated carboxylic acid)
	912	OH...O out of plane deformation

The PMA synthesized was also studied with MALDI/TOF mass spectroscopy. The assignment of the mass peaks is summarized in Table 3.

Table 3. The assignment of the mass peaks in the MALDI/TOF mass spectrum of PMA.

Mass Peak	Assignment		
	degree of polymerization (PMA)	addition to PMA	theoretical mass
1,742	15	-	1,740
1,856	16	-	1,856
2,027	17	K+H <sub>2</sub> O	2,029
2,145	18	K+H <sub>2</sub> O	2,145
2,315	20	-	2,320
2,714	23	2 Na	2,714
2,886	24	SO <sub>4</sub>	2,880

10 Gel permeation chromatography with a multi angle laser light scattering detector (GPC/MALLS) was used to measure the molecular weight distribution of PMA. Presented in Figures 4A and 4B are the GPC chromatograms of PMA with refractive index (RI) detector and the light scattering (LS) detector at 90°, respectively. Figure 5 shows the curve of cumulative weight fraction as a function of the molar mass for PMA. One

15 observes that the molecular weight of the PMA are between 300-4,000 with 80% (w/w) of the polymer in the range 300-3,000. The weight average molecular weight ( $M_w$ ) of PMA is  $1.62 \times 10^3$  and the number average molecular weight ( $M_n$ ) is 830. Therefore, the polydispersity of the molecular weight ( $M_w/M_n$ ) is 1.95. Based on the FT-Raman spectroscopy and the GPC-MALLS data, MA was believed to homopolymerize in the

20 presence of the  $\text{NaH}_2\text{PO}_2/\text{K}_2\text{S}_2\text{O}_8$  initiation system.

#### Polymerization of FA

25 10g  $\text{NaH}_2\text{PO}_2$  was added to 70 ml saturated aqueous solution of FA with excess FA present (total FA: 18.6g; FA concentration: 0.7%). The Raman spectrum of the solution is presented in Figure 6A. The bands at 1717 and 1660  $\text{cm}^{-1}$  are due to the stretching modes of carboxylic acid carbonyl and C=C of FA, respectively, and the intense band at 1045  $\text{cm}^{-1}$  is the P=O stretching mode of  $\text{NaH}_2\text{PO}_2$  (Figure 6A). The unsaturated =C-H stretching mode of

FA is not visible in the spectrum due to the low concentration of FA. The mixture of FA and  $\text{NaH}_2\text{PO}_2$  is stirred to form a slurry, in which most of FA is not soluble. The temperature of the slurry was increased to  $90^\circ\text{C}$ .  $2.5\text{g K}_2\text{S}_2\text{O}_8$  was added to the slurry under stirring.

Vigorous reaction takes place and  $\text{K}_2\text{S}_2\text{O}_8$  quickly dissolves as soon as  $\text{K}_2\text{S}_2\text{O}_8$  was added.

5 The reaction mixture was kept at  $95^\circ\text{C}$  for 5 min. The spectrum of the reaction mixture is shown in Figure 6B. One observes that a band at  $2940\text{ cm}^{-1}$  due to saturated C-H stretching appears and the intensity of the band at  $1660\text{ cm}^{-1}$  due to the stretching mode of C=C of FA relative to that of the carbonyl band at  $1717\text{ cm}^{-1}$  is significantly reduced in the spectrum (Figure 6B). The band at  $1660\text{ cm}^{-1}$  almost completely disappears after the reaction mixture  
10 was kept at  $82^\circ\text{C}$  for 30 min (Figure 6C). The data indicate that most of the FA monomers polymerize to form poly(fumaric acid) (PFA) within the first 5 min after the initiator is added to the mixture, and the polymerization is complete after 30 min.

#### Polymerization of IA

15 24.3g IA and 8.6g  $\text{NaH}_2\text{PO}_2$  are added to 64.2 ml  $\text{H}_2\text{O}$ , and the temperature of the reaction mixture was increased from room temperature to  $95^\circ\text{C}$ . The Raman spectrum of the IA/ $\text{NaH}_2\text{PO}_2$  mixture is presented in Figure 7A. The stretching modes of unsaturated =C-H<sub>2</sub> of IA are shown at  $3117$  and  $3007\text{ cm}^{-1}$  and the stretching mode of C=C is at  $1642\text{ cm}^{-1}$ , whereas the stretching mode of the saturated C-H of IA appears at  $2936\text{ cm}^{-1}$  in Figure 7A. One third of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  by total weight of the final mixture was added to the IA/ $\text{NaH}_2\text{PO}_2$   
20 mixture as soon as the temperature reaches  $95^\circ\text{C}$ . The intensities of the bands at  $3117$ ,  $3007$  and  $1642\text{ cm}^{-1}$  due to IA are significantly reduced 10 min after the addition of  $\text{K}_2\text{S}_2\text{O}_8$  (Figure 7B). The second portion of the  $\frac{1}{3}$  of 2.9%  $\text{K}_2\text{S}_2\text{O}_8$  was added and the mixture was kept at  $95^\circ\text{C}$  for another 10 min (Figure 7C). The last portion of  $\text{K}_2\text{S}_2\text{O}_8$  was added and the polymerization continues at  $95^\circ\text{C}$  for the third 10 min (Figure 7D). One observes that the  
25 band at  $1642\text{ cm}^{-1}$  due to C=C of IA almost disappears and the two bands at  $3117$  and  $3007\text{ cm}^{-1}$  due to stretching modes of unsaturated =CH<sub>2</sub> of IA are no longer visible in the spectrum (Figure 7D). The band at  $1642\text{ cm}^{-1}$  entirely disappears when the total polymerization time reaches 60 min, thus indicating that the conversion from monomer to polymer is complete (Figure 7E).

Polymerization of MA and IA on cotton fabric

In previous research, it was determined that polycarboxylic acids having their carboxyl groups bonded to the adjacent carbons of their molecular backbones form 5-membered cyclic anhydrides on cotton fabric under the curing conditions (Yang, C.Q. (1993), "Infrared Spectroscopy Studies of the Cyclic Anhydride as the Intermediate for the Ester Crosslinking of Cotton Cellulose by Polycarboxylic Acid, I: Identification of the Cyclic Anhydride Intermediate," J. Polym. Sci., Polym. Chem. Ed. **31**:1187-1193; Yang, C.Q. and Wang, X. (1996), "Formation of Cyclic Anhydride Intermediates and Esterification of Cotton Cellulose by Multifunctional Carboxylic Acids: An Infrared Spectroscopy Study," Textile Res. J. **66**:595-603; Yang, C.Q. and Wang, X. (1996), "Infrared Spectroscopy Studies of the Cyclic Anhydride as the Intermediate for the Ester Crosslinking of Cotton Cellulose by Polycarboxylic Acids," II: Comparison of Different Polycarboxylic Acids," J. Polym. Sci., Polym. Chem. Ed. **34**:1573-1580). Presented in Figure 8A is the infrared spectrum of the cotton fabric treated with 6% MA. The band at  $1726\text{ cm}^{-1}$  in Figure 8A is due to the stretching mode of carboxylic acid carbonyl. Two bands at  $1849$  and  $1779\text{ cm}^{-1}$  emerge in the spectrum when the treated fabric was cured at  $140^{\circ}\text{C}$  for 2 min (Figure 8B). These two bands are due to the symmetric and asymmetric stretching modes of MAN formed under the curing condition, and they appear to be sharp in the difference spectrum (Figure 8C). The spectra of the fabric treated with 6.7% IA before and after curing at  $200^{\circ}\text{C}$  for 2 min are shown in Figures 9A and 9B, respectively. The two bands  $1842$  and  $1769\text{ cm}^{-1}$  due to the cyclic anhydride carbonyl of IA are also distinct in the difference spectrum (Figure 9C).

Two explicit carbonyl bands at  $1853$  and  $1781\text{ cm}^{-1}$  due to the 5-membered cyclic anhydride intermediate are seen in the spectrum of the cotton fabric treated with 6% PMA and cured at  $180^{\circ}\text{C}$  for 2 min (Figures 10B). The two anhydride carbonyl bands in the difference spectrum of the PMA-treated fabric (Figure 10C) are much broader than those of MA and IA (Figures 8C and 9C, respectively). For PMA, an anhydride may form next to another anhydride in its molecular chain or it may form next to a free carboxyl group, and the different chemical environments of the 5-membered anhydride intermediates of PMA causes band broadening in the infrared spectra. The anhydride of PMA also absorbs at higher

frequency than those of MA and IA, because the conjugation of the carbonyl and the alkene double bond of MA and IA lowers the anhydride carbonyl stretching bands frequencies (Bellamy, K.J. (1975), "The Infrared Spectra of Complex Molecules, 3<sup>rd</sup> ed., Chapman and Hall, London, pp. 144-145; Clothup, N.B. et al. (1990), "Introduction to Infrared and Raman Spectroscopy," Ch. 9, Academic Press, San Diego, CA, pp. 310-312).

In another experiment, the cotton fabric was treated with 6.7 % IA, 4.0% NaH<sub>2</sub>PO<sub>2</sub> in combination with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> of different concentrations (0.00, 0.25, 0.50, 1.00 and 2.00 %). The fabric samples were then cured at 180°C for 2 min. The difference spectra of the cotton fabric samples thus treated (the fabric after curing minus that before curing) are presented in Figure 11. Without K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> on the fabric, the anhydride carbonyl has its symmetric and asymmetric stretching modes at 1843 and 1768 cm<sup>-1</sup>, respectively, in the difference spectrum (Figure 11A). These two bands are obviously due to the anhydride of IA, thus indicating that IA does not polymerize on the fabric under the curing condition (Figure 11A). When the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration increases to 0.5%, the two anhydride stretching bands shift from 1843/1768 to 1847/1777 cm<sup>-1</sup>, and the band at 1847 cm<sup>-1</sup> becomes apparently broader (Figure 11C). The shift of the anhydride stretching bands to higher frequencies and the broadening of the band at 1847 cm<sup>-1</sup> are indications of polymerization of IA on the fabric. The anhydride stretching bands shift to even higher frequencies as the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration increases. When the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration increases to 2.0%, the two anhydride carbonyl bands appear at 1854 and 1780 cm<sup>-1</sup>, which are similar to those of the anhydride formed by PMA (1854/1783 cm<sup>-1</sup>). Thus, the infrared spectroscopy data show that the anhydride formed on the fabric treated with 6.7% IA, 4% NaH<sub>2</sub>PO<sub>2</sub>, and 2.0% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and cured at 180°C for 2 min is that of a saturated polycarboxylic acid (Figure 11E). This is a piece of direct evidence to prove the in-situ polymerization of IA on the cotton fabric under a elevated temperature. The data reveal that the in-situ polymerization is significantly effected by the amount of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> present in the system.

In another experiment, cotton fabric was treated with 6% MA, 6.7% IA, 4% NaH<sub>2</sub>PO<sub>2</sub> in combination with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> of different concentrations, and cured at 180°C for 2 min. The

amount of the free monomers on the treated fabric was measured by quantitative determination of the alkene double bond concentration on the treated fabric with redox titration. The percentage of the free monomers on the fabric is presented as function of the  $K_2S_2O_8$  concentration in the acids solution (Figure 12). One observes that the amount of the free monomers decreases sharply as the  $K_2S_2O_8$  concentration increases. The change in free monomer concentration on the cotton fabric treated with MA and IA shown in Figure 12 is consistent with the infrared spectroscopy data presented in Figure 11.

In order to confirm the existence of the polymers formed in-situ on the cotton fabric, FT-IR spectroscopy was used to investigate the formation of the 5-membered cyclic anhydride on the treated fabric after hydrolysis. The cotton fabric was treated with 6.7% IA, 4%  $NaH_2PO_2$  and 2%  $K_2S_2O_8$ , and cured at  $180^\circ C$  for 2 min. The treated fabric was subjected to 10 washing cycles with warm water ( $50-60^\circ C$ ) and a detergent (AATCC standard detergent 124), and then treated with 0.1 M acetic acid to convert carboxylate ions to carboxylic acid on the fabric (Figure 13A). The fabric thus treated was finally heated at  $180^\circ C$  for 2 min (Figure 13B). The two bands at  $1856$  and  $1781\text{ cm}^{-1}$  due to the anhydride carbonyl of a saturated polycarboxylic acid appear in the difference spectrum (Figure 14C). Similarly, two bands at  $1855$  and  $1782\text{ cm}^{-1}$  emerge in the difference spectrum of the cotton fabric treated with 6.0% MA, 4.0%  $NaH_2PO_2$  and 2.0%  $K_2S_2O_8$ , cured at  $180^\circ C$  for 2 min, subjected to 10 washing cycles, and finally heated at  $180^\circ C$  for 2 min. Those bands observed are believed due to the anhydrides of the PIA and PMA on the treated cotton fabric samples.

When cotton fabric treated with IA or MA and cured at  $180^\circ C$  for 2 min was washed in warm water, the free MA or IA formed due to hydrolysis are removed from the fabric. Those MA and IA molecules as monomers bonded to the cotton fabric through ester linkages are not able to form cyclic anhydrides because each bonded IA or MA molecule has only one free carboxylic acid group. Only when MA and IA polymerize on the fabric, the hydrolysis of the ester linkages results in formation of multiple free carboxyl groups in the polymer, which can form 5 membered cyclic anhydride upon exposure to elevated temperatures. Therefore, formation of the cyclic anhydride on the treated fabric after hydrolysis is an

additional piece of evidence to prove that IA and MA polymerize on the cotton fabric. The homopolymer and copolymer of MA and IA formed in-situ from the fabric was removed using alkaline hydrolysis and the molecular weight of the polymers was determined using a time-of-flight mass spectrometer and the weight-averaged molecular weight was determined to be around 2000 by multiple angle laser light scattering (Yang, C.Q. and Lu, Yun (2000) Textile Res. J. 70(4) 359-362).

The performance of the treated cotton fabric was evaluated. The WRA (wrinkle recovery angle) of the cotton fabric treated with 6.7% IA and 4.0%  $\text{NaH}_2\text{PO}_2$  in combination with  $\text{K}_2\text{S}_2\text{O}_8$  of different concentrations is shown in Table 4. The WRA of the cotton fabric increases from 200 to 241 degree when the fabric is treated without  $\text{K}_2\text{S}_2\text{O}_8$ . It increases further to 262 degree when 0.25%  $\text{K}_2\text{S}_2\text{O}_8$  is present in the finishing solution. WRA increases moderately as the  $\text{K}_2\text{S}_2\text{O}_8$  concentration increases in the system. The effect of  $\text{K}_2\text{S}_2\text{O}_8$  on the performance of the treated cotton fabric becomes more striking after the fabric is subjected to 10 washing cycles in warm water. The fabric treated with 6.7% IA and 4.0%  $\text{NaH}_2\text{PO}_2$  without  $\text{K}_2\text{S}_2\text{O}_8$  shows WRA of 227 degree. When 0.25%  $\text{K}_2\text{S}_2\text{O}_8$  is presented in the finishing system, however, the WRA increases to 262 degree.

TABLE 4. Wrinkle recovery angles (w + f, °) of cotton fabrics treated with IA or MA and 4.0%  $\text{NaH}_2\text{PO}_2$  in combination with different concentrations of  $\text{K}_2\text{S}_2\text{O}_8$  and cured at 180°C for 2 minutes

K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> concentration, %, w/w	6.7% IA		6.0% MA	
	Before washing	After ten washing cycles	Before washing	After ten washing cycles
0.00	241	227	247	216
0.25	262	262	258	237
0.50	265	266	252	244
1.00	271	270	264	252
2.00	269	270	260	261
Control	200	---	200	---



The WRA of the cotton fabric treated with 6.0% MA and 4.0%  $\text{NaH}_2\text{PO}_2$  in combination with  $\text{K}_2\text{S}_2\text{O}_8$  of different concentrations is also included in Table 4. The WRA of the treated fabric increases when  $\text{K}_2\text{S}_2\text{O}_8$  is present in the finish solution. One observes that the  $\text{K}_2\text{S}_2\text{O}_8$  concentration has a profound impact on the WRA of the MA-treated fabric after 10 washing cycles (Table 4). The significant improvement in the fabric wrinkle-resistance in the presence of  $\text{K}_2\text{S}_2\text{O}_8$  in the finish system and the effect of  $\text{K}_2\text{S}_2\text{O}_8$  concentration on the wrinkle-resistance of the treated fabric are indicative of the in-situ polymerization of IA and MA on the fabric and ester crosslinking of the cotton fabric by the polymers, and are consistent with all the data presented above.

Presented in Table 5 are the WRA, DP rating and mechanical strength of the cotton fabric treated with formations containing different acids and different  $\text{K}_2\text{S}_2\text{O}_8$  concentrations. DP rating is a standard rating system for fabric smoothness with 5 being the best and 1 being the worst with many wrinkles. In the table, w, f and w + f take their standard meaning as known in the art with w being the warp direction in fabric, and f indicating filling direction. w + f is the sum of w and f. The performance of the fabric treated with 1,2,3,4-butanetetracarboxylic acid (BTCA) is also included for the purpose of comparison. The cotton fabric treated with the finish solutions containing IA, MA, and the combination of IA and MA, in the presence of 2%  $\text{K}_2\text{S}_2\text{O}_8$  (Formulation 1-3 in Table 5) show high level of wrinkle resistance and smooth appearance. The WRA and DP rating of the treated fabric during 20 home laundry washing cycles is presented in Table 6. The fabric treated with the three formulations also have high levels of laundry durability. IA is obviously the most effective finishing agent. Even though MA is the least efficient one among the three finishing formulations, as indicated by the relatively lower wrinkle recovery angle, it still provides the fabric with satisfactory wrinkle-resistance, smoothness and laundering durability (Table 5).

TABLE 5. Performance of cotton fabric treated with different finishing systems and cured at 180°C for 2 minutes

Finish formulation	DP rating	WRA, w + f, °	Tearing strength, lbs.		Breaking strength, lbs.		Flex abrasion, cycles	
			W	F	W	F	W	F
(1) 9% MA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.0	285	1.8	0.9	36	16	58	35
(2) 10% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.0	293	1.9	0.9	37	15	49	20
(3) 4.5% MA, 5% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.2	290	1.8	0.9	37	16	63	37
(4) 4.5% MA, 5% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 0.1% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.0	272	1.7	1.2	43	21	165	132
(5) 6% BTCA, 4% NaH <sub>2</sub> PO <sub>2</sub>	3.3	300	1.8	1.1	37	17	88	50
Control	---	200	1.8	1.3	54	41	537	246

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All the formulations contain 3% high density polyethylene fabric softener.

TABLE 6. Conditioned wrinkle recovery angle and durable press rating of treated cotton fabric after different numbers of home laundering cycles

Finish formulations	Wrinkle recovery angle, w + f, °, number of washing cycles					DP rating, number of washing cycles				
	0	5	10	20	20	0	5	10	20	20
(1) 9% MA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	285	281	270	250	250	3.0	3.0	3.0	3.0	2.5
(2) 10% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	293	294	284	274	274	3.2	3.2	3.0	3.0	3.0
(3) 4.5% MA, 5% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 2% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	290	283	270	266	266	3.2	3.1	3.0	3.0	3.0
(4) 4.5% MA, 5% IA, 4% NaH <sub>2</sub> PO <sub>2</sub> , 0.1% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	272	249	227	213	213	3.0	3.0	2.5	2.5	2.3
(5) 6% BTCA, 4% NaH <sub>2</sub> PO <sub>2</sub>	300	290	288	281	281	3.3	3.3	3.3	3.3	3.3

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The mechanical strength of the three treated fabric samples is similar to or somewhat lower than that of the BTCA-treated fabric, probably because the acids concentration of the three formations is higher than that of BTCA, and therefore those three formulations causes more acid degradation of cellulose than that of BTCA.

5 For free-radical chain polymerization carried out in a liquid state, such as solution or emulsion polymerization, the initiator concentration used is usually less than 1% of monomer. In a paper by Choi, the  $K_2S_2O_8$  concentration in the finish system was 1.5% of the weight of the monomers (Choi, H.-M. (1992), "Nonformaldehyde Polymerization-Crosslinking treatment of Cotton Fabrics for Improved Strength Retention," Textile Res. J. 10 **62**:614-618). Here, however, the  $K_2S_2O_8$  concentration was found to have a profound effect on the in-situ polymerization, and the  $K_2S_2O_8$  concentration required to achieve the in-situ polymerization with significant quantity is much higher than the concentrations conventionally used for free-radical chain polymerization.

In order to verify the previous observation based on the performance of the treated 15 fabric, a formulation containing only 0.1%  $K_2S_2O_8$ , approximately 1% of that of the monomers was included (Formulation 4 in Table 5). The cotton fabric treated with this formulation shows WRA of 272 degree before washing. However, the fabric wrinkle resistance diminishes rapidly during the washing process, and the WRA reduces to 213 degree after 20 washing cycles (Table 6). The poor laundry durability of the treated fabric at a 20 low  $K_2S_2O_8$  concentration level indicates inadequate polymerization of the monomers and insufficient crosslinking of cotton cellulose. It also explains why the fabric treated with 0.1%  $K_2S_2O_8$  shows higher mechanical strength (Table 5).

Although the description above contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some 25 of the presently-preferred embodiments of this invention. For example, the methods of the invention may be used to polymerize other carboxylic acids. Thus, the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the

examples given. Modifications that are within the scope of the invention are known to the art without undue experimentation using the teachings described herein. All references cited herein are hereby incorporated by reference to the extent not inconsistent with the disclosure herewith.

## CLAIMS

What is claimed is:

1. A method of polymerizing at least one olefinically unsaturated compound containing at least two carboxyl groups which comprises:
  - 5 (a) mixing a phosphorous-containing reducing agent, one or more olefinically unsaturated monomers which contain at least two carboxyl groups, and a free radical generator to form a mixture; and
  - (b) subjecting said mixture to polymerization conditions.
- 10 2. The method of claim 1 wherein said polymerization conditions comprise the application of heat.
3. The method of claim 2 wherein said heat is between about 40 and about 100 °C.
4. The method of claim 3 wherein said heat is between about 50 and about 85 °C.
5. The method of claim 1, wherein said mixture further comprises water as a solvent.
- 15 6. The method of claim 1, wherein said monomer is present at between about 1 and about 50% of the total weight of the mixture.
7. The method of claim 1, wherein said reducing agent is present at between about 1 to about 15% of the total weight of the mixture.
8. The method of claim 1, wherein the mole ratio of said free radical generator:reducing agent is between about 0.1:10 to about 10:0.1.
- 20 9. The method of claim 1, wherein the mole ratio of said free radical generator:reducing agent is between about 0.1:1 to about 1:1.

10. The method of claim 1, wherein said monomer is one or more of the group consisting of maleic acid, fumaric acid, itaconic acid, citraconic acid, cis-aconitic acid, trans-aconitic acid and 3-butene-1,2,3-tricarboxylic acid.
11. The method of claim 1, wherein more than one different monomer is used.
- 5 12. A method of forming polymers on cellulose substrates comprising:
  - (a) immersing a substrate in a solution comprising at least one monomer that contains at least two carboxyl groups at a monomer concentration of between about 2 and about 15% of the total weight of solution, said solution also comprising a free radical generator at a concentration of between about 1 and  
10 about 4 % of the total weight of solution and a phosphorous-containing reducing agent at a concentration of between about 1 and about 10 % of the total weight of solution; and
  - (b) curing the substrate.
13. The method of claim 12, wherein said free radical generator is present at a  
15 concentration of about 2% of the total weight of solution.
14. The method of claim 12, wherein said phosphorous-containing reducing agent is present at a concentration of about 4 % of the total weight of solution.
15. The method of claim 12, wherein said curing step occurs at a temperature of about 150 to about 200°C.
- 20 16. The method of claim 12, wherein said monomer is one or more selected from the group consisting of: maleic acid, fumaric acid, itaconic acid, citraconic acid, cis-aconitic acid, trans-aconitic acid and 3-butene-1,2,3-tricarboxylic acid.

17. The method of claim 12, wherein said solution also contains one or more emulsifiers at a concentration of between about 0.05 and about 0.5 % of the total weight of solution.
18. The method of claim 12, wherein said substrate is selected from the group consisting of cotton, rayon and cotton-polyester blends.
19. The method of claim 12, wherein said substrate is nonwoven.
20. A polymerization system comprising:  
a free radical generator at a concentration of between about 1 to about 4% of the total weight of the system and a phosphorous-containing reducing agent at a concentration of between about 1 to about 25% of the total weight of the system and an aqueous solvent.
21. The system of claim 20, wherein said free radical generator is selected from the group consisting of:  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$ .
22. The system of claim 20, wherein said reducing agent is selected from the group consisting of:  $\text{NaH}_2\text{PO}_2$  and  $\text{Na}_2\text{HPO}_3$ .
23. The system of claim 20, wherein said reducing agent is present at a concentration of between about 1 to 10% of the total weight of the system.
24. The system of claim 20, wherein said free radical generator is present at a concentration above about 2% of the total weight of the system.
25. The system of claim 20, wherein the mole ratio of said free radical generator:phosphorous-containing reducing agent is between about 0.1:10 to about 10:0.1.

26. The system of claim 20, further comprising an olefinically unsaturated compound containing at least two carboxyl groups at a concentration of between about 1 to about 50% of the total weight of the system.



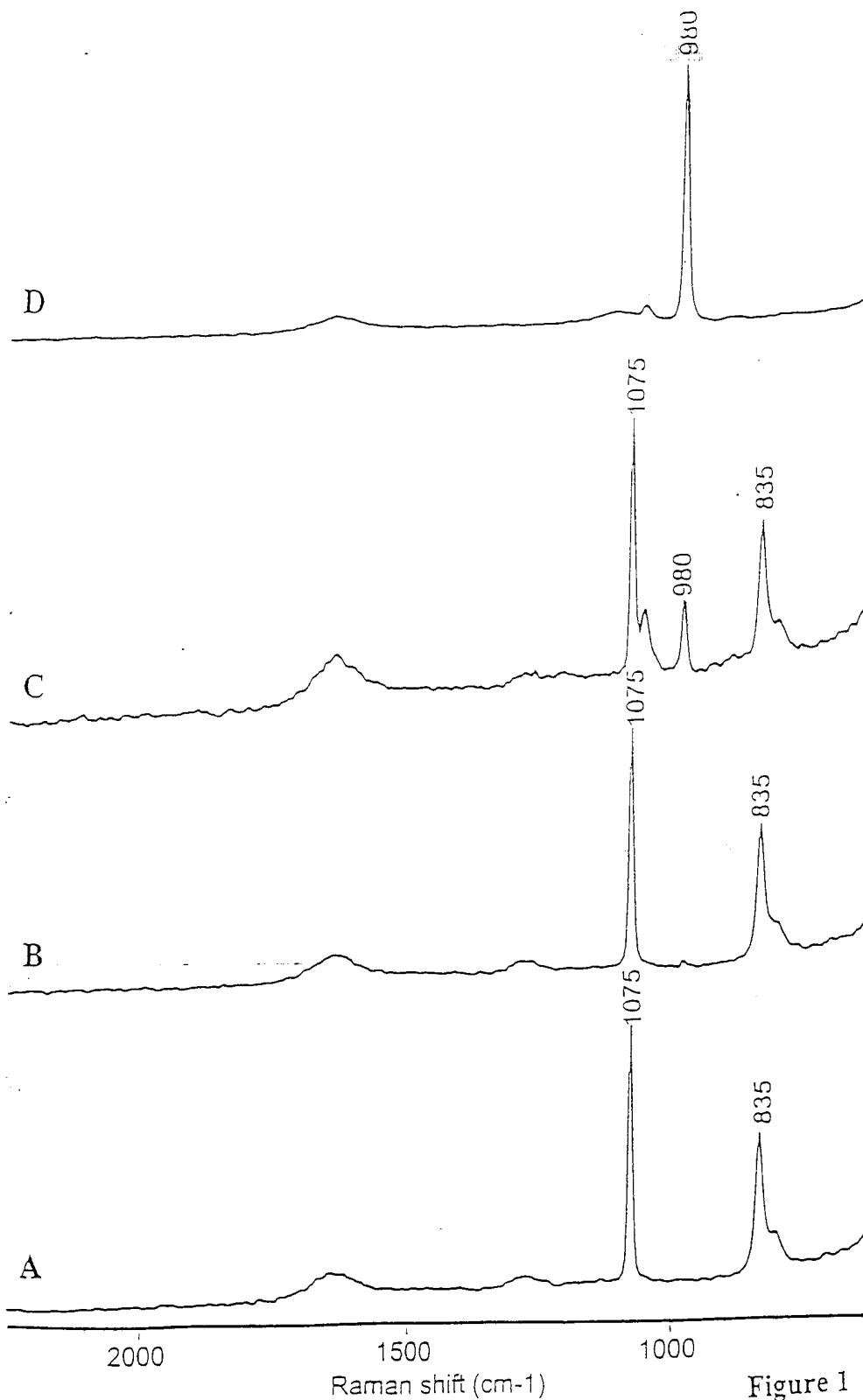


Figure 1

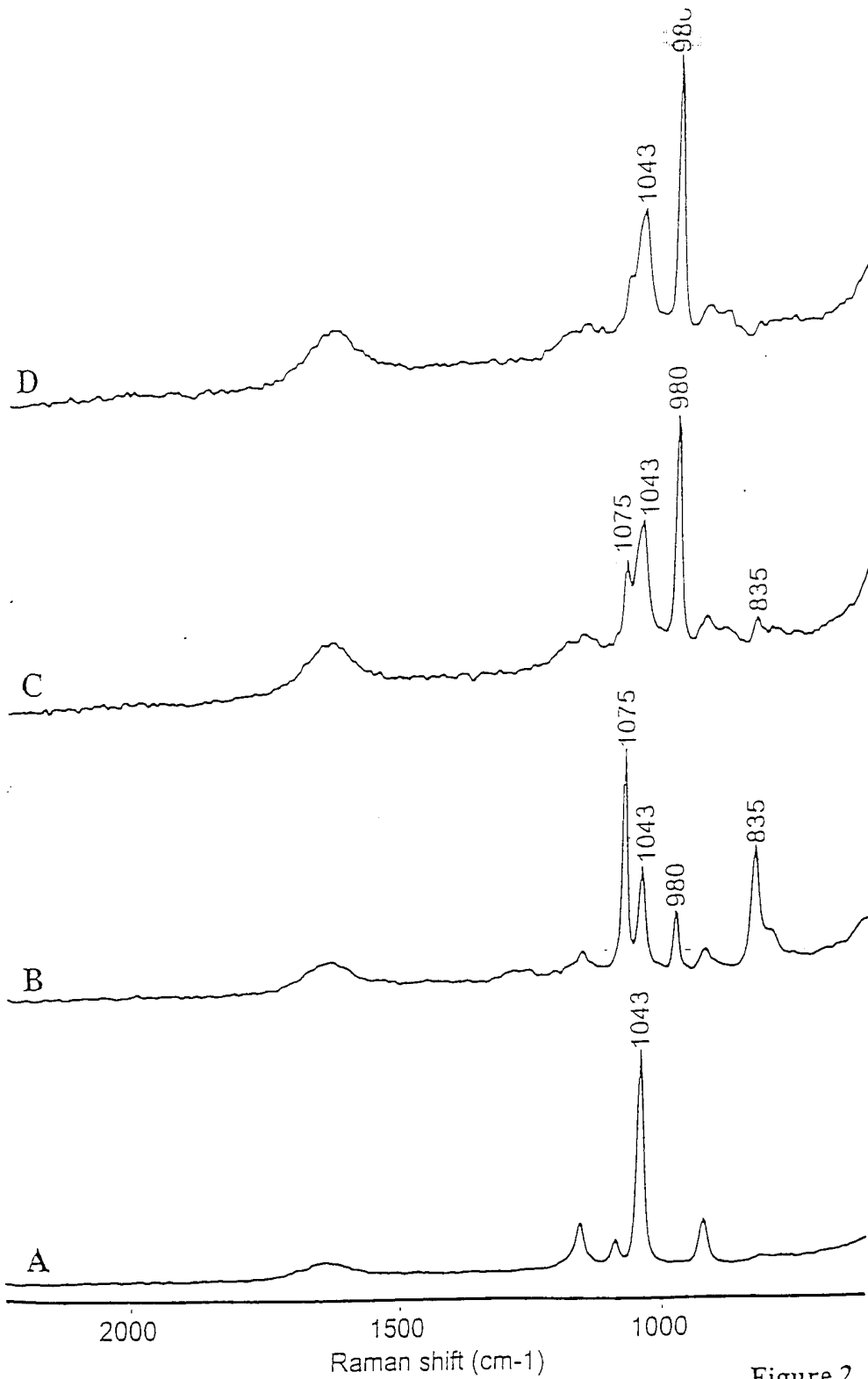


Figure 2

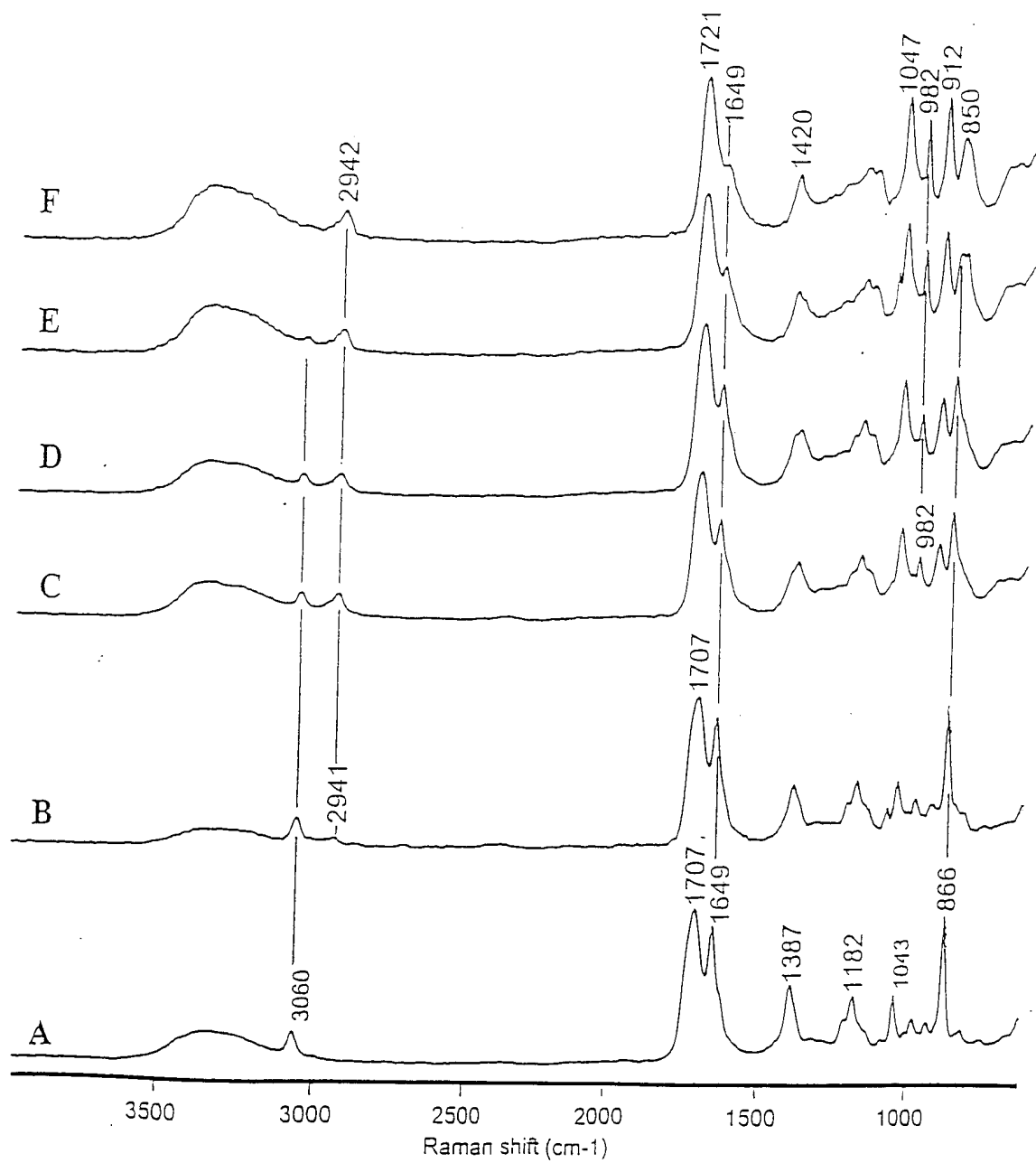


Figure 3

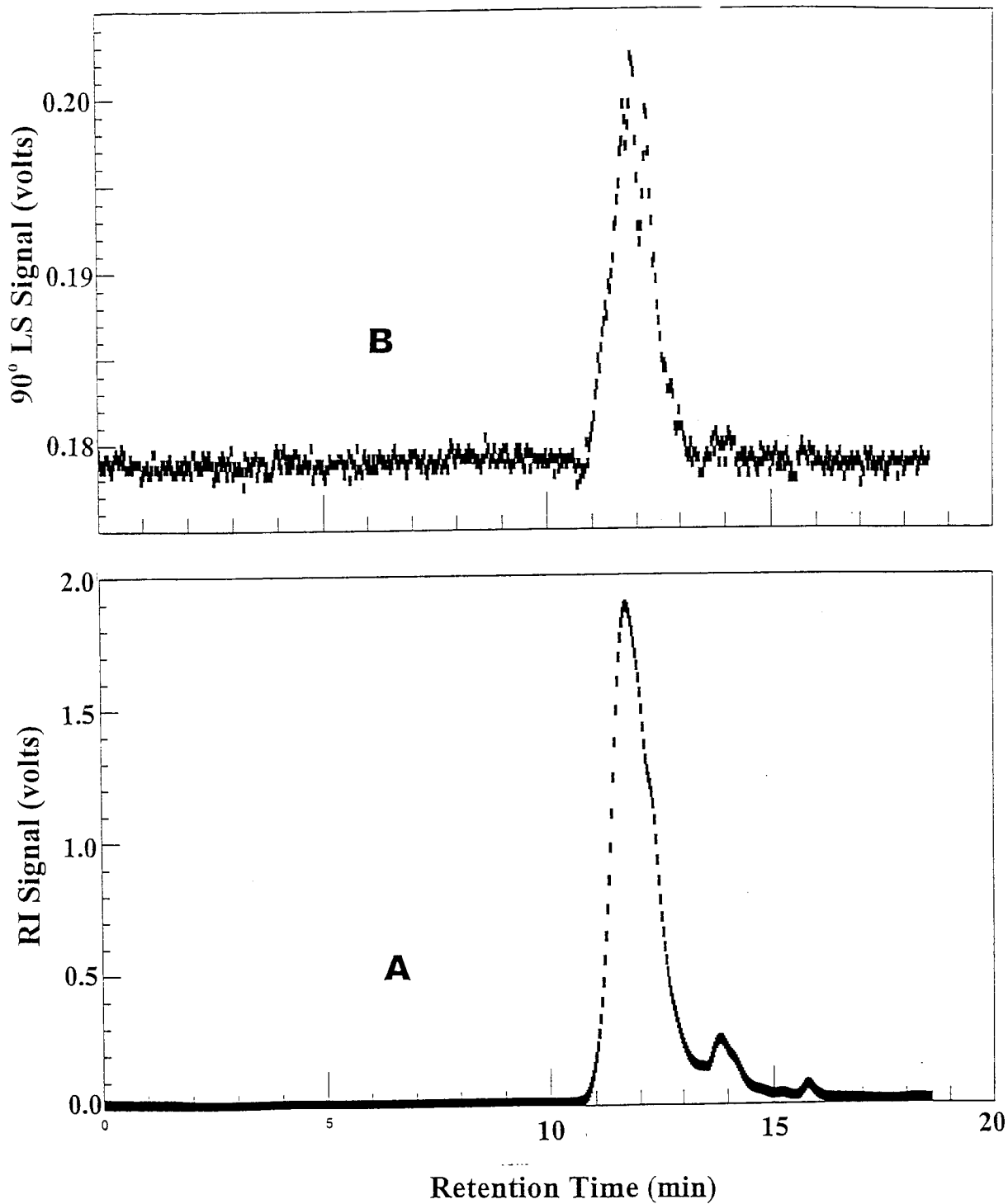


Fig. 4

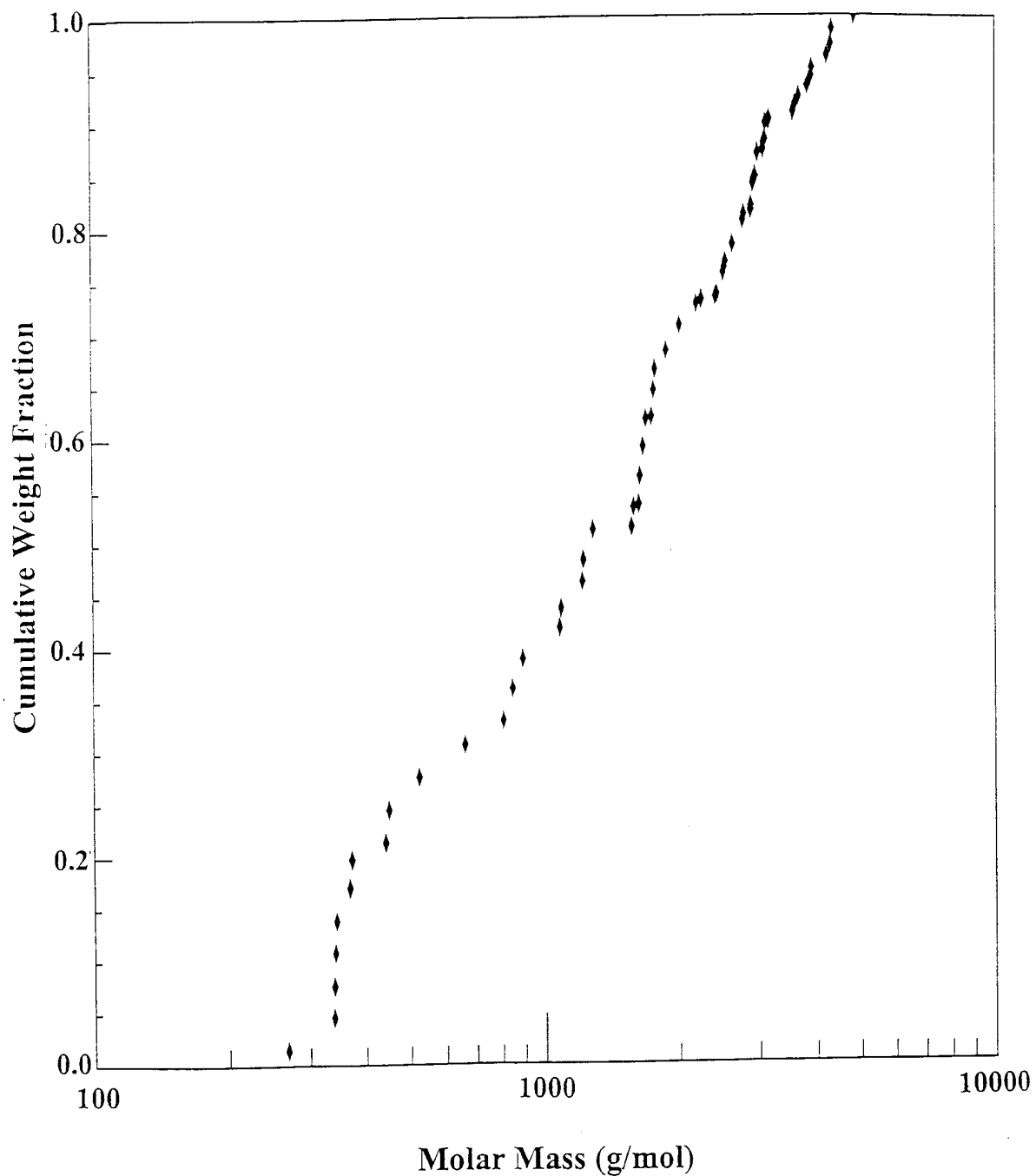


Fig. 5

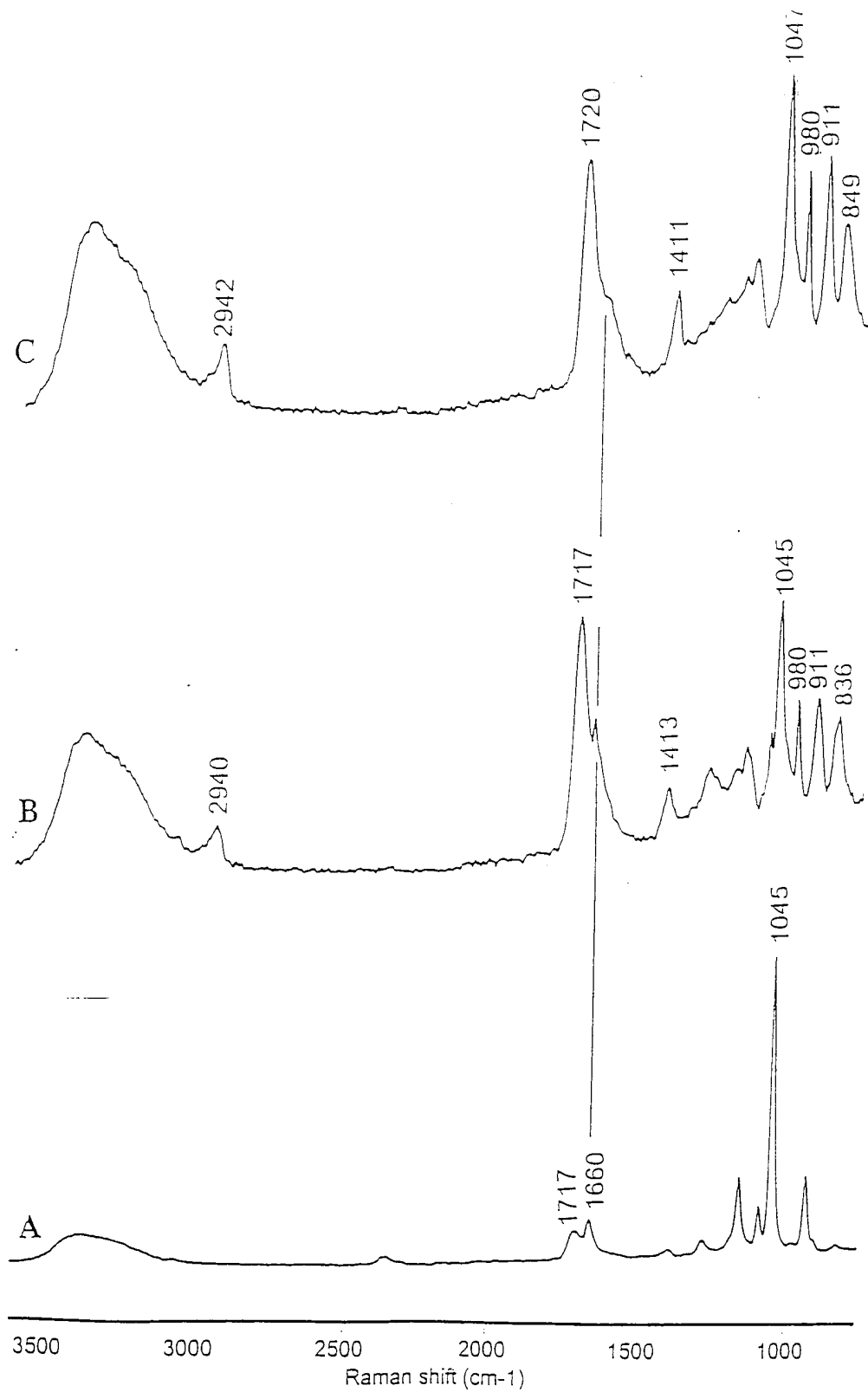


Figure 6

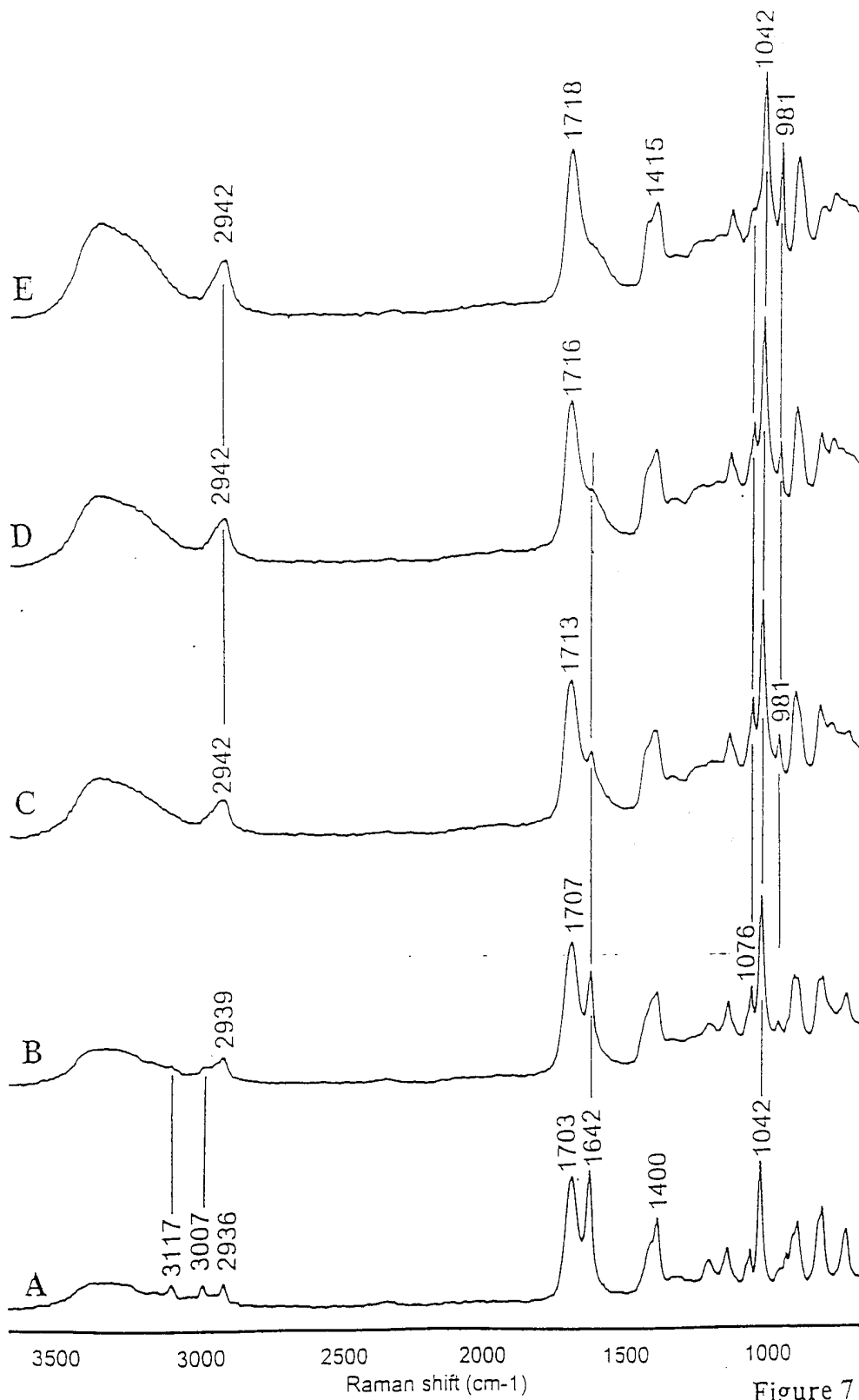


Figure 7

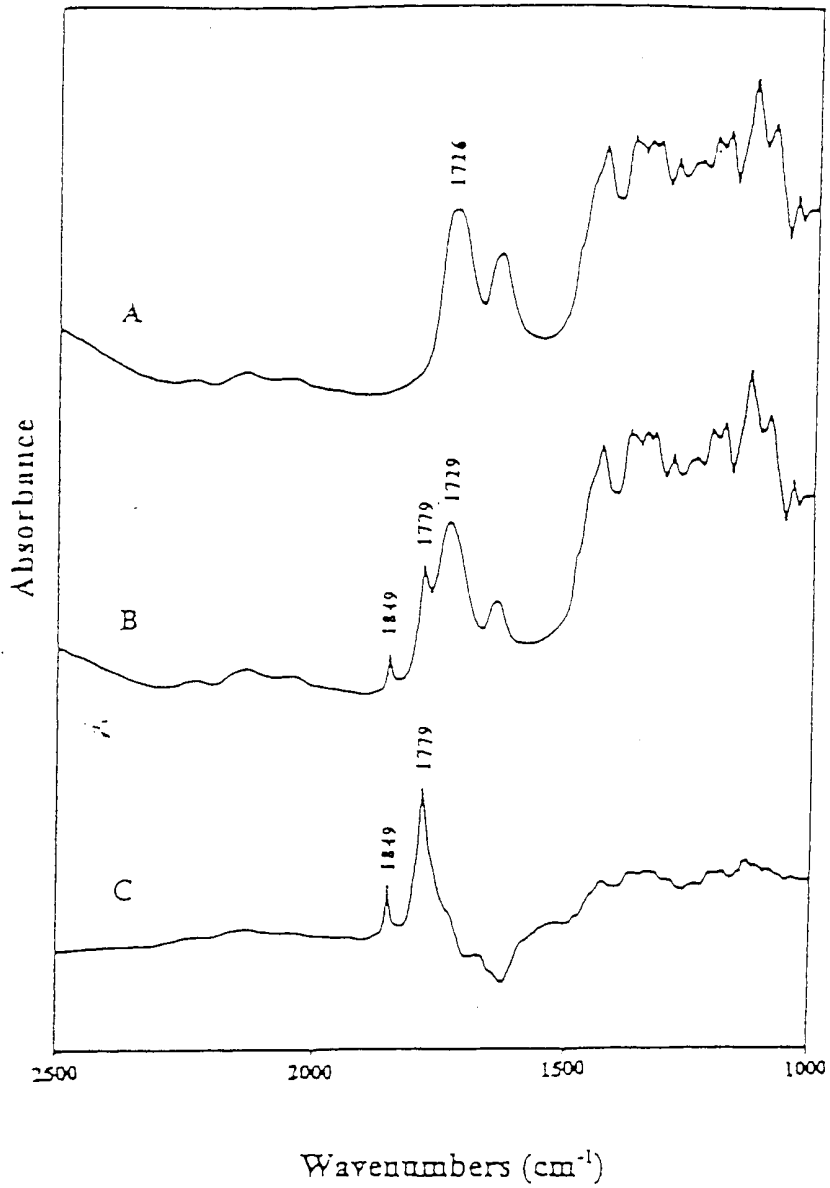


Figure 8



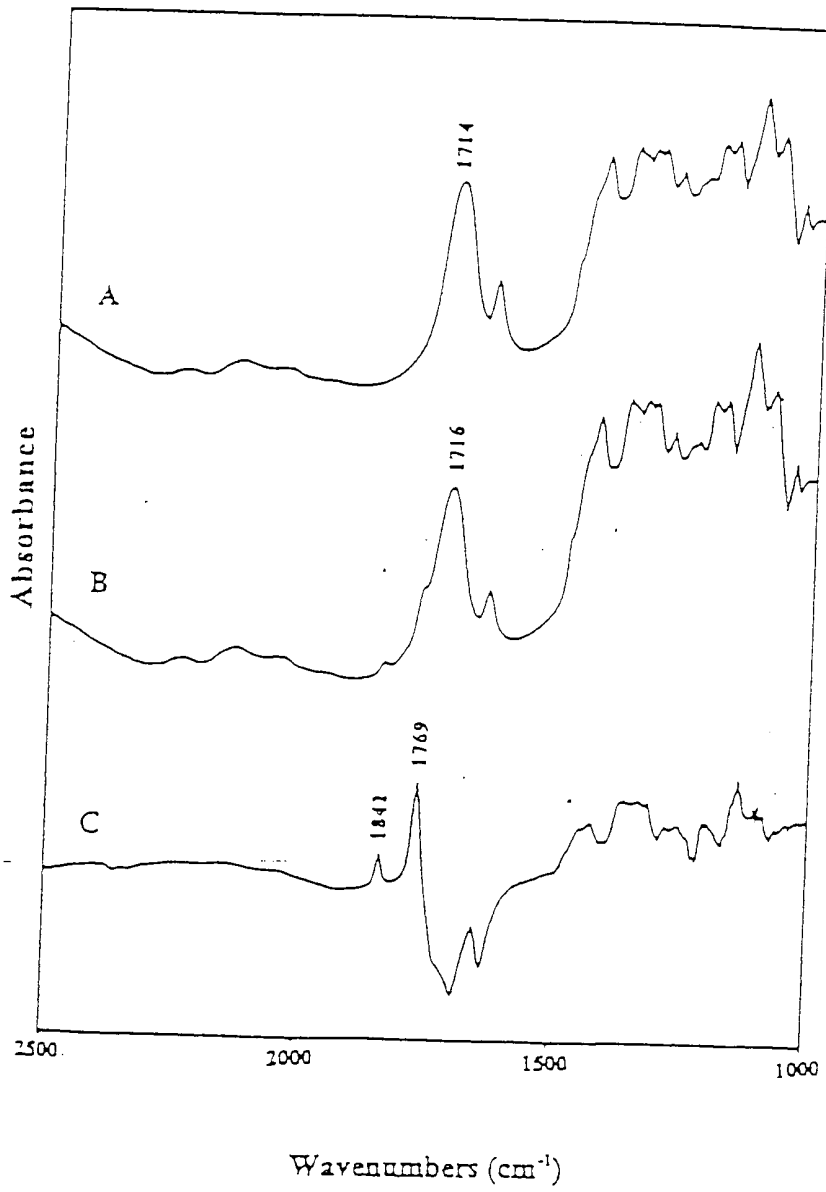


Figure 9

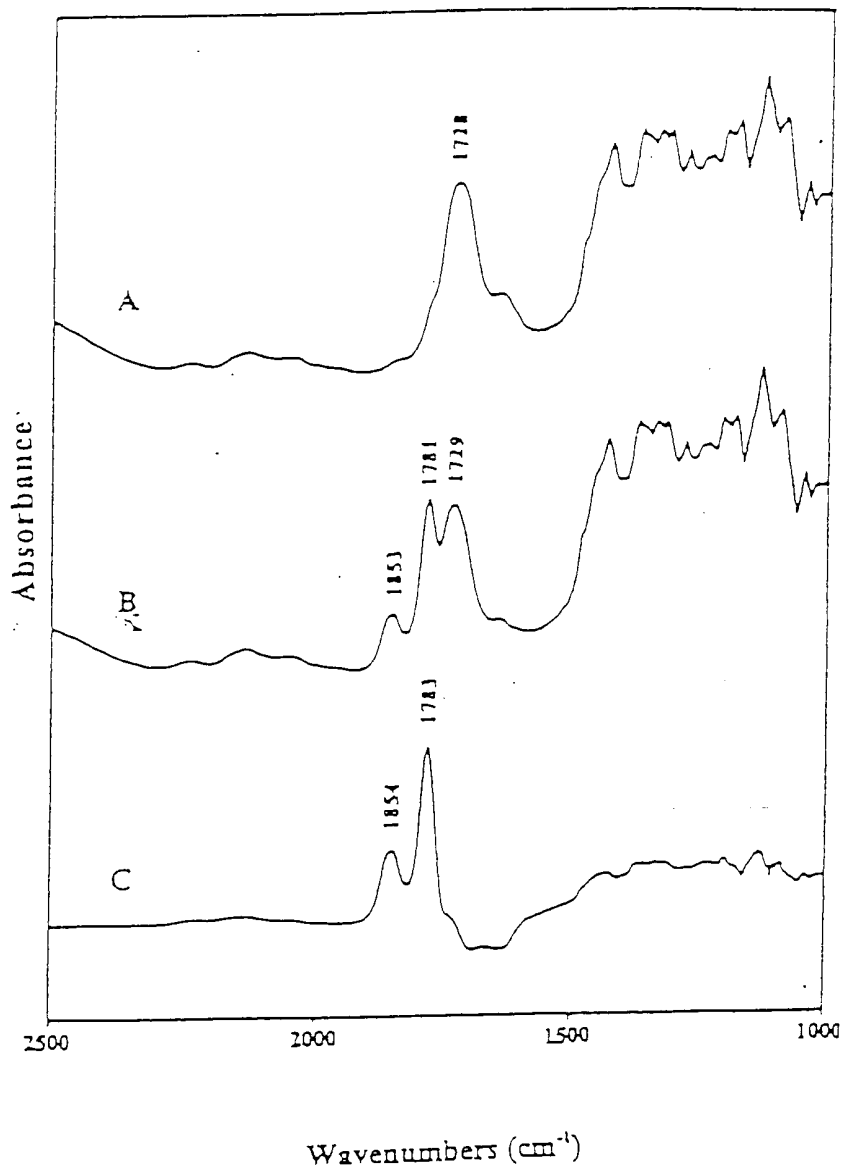


Figure 10

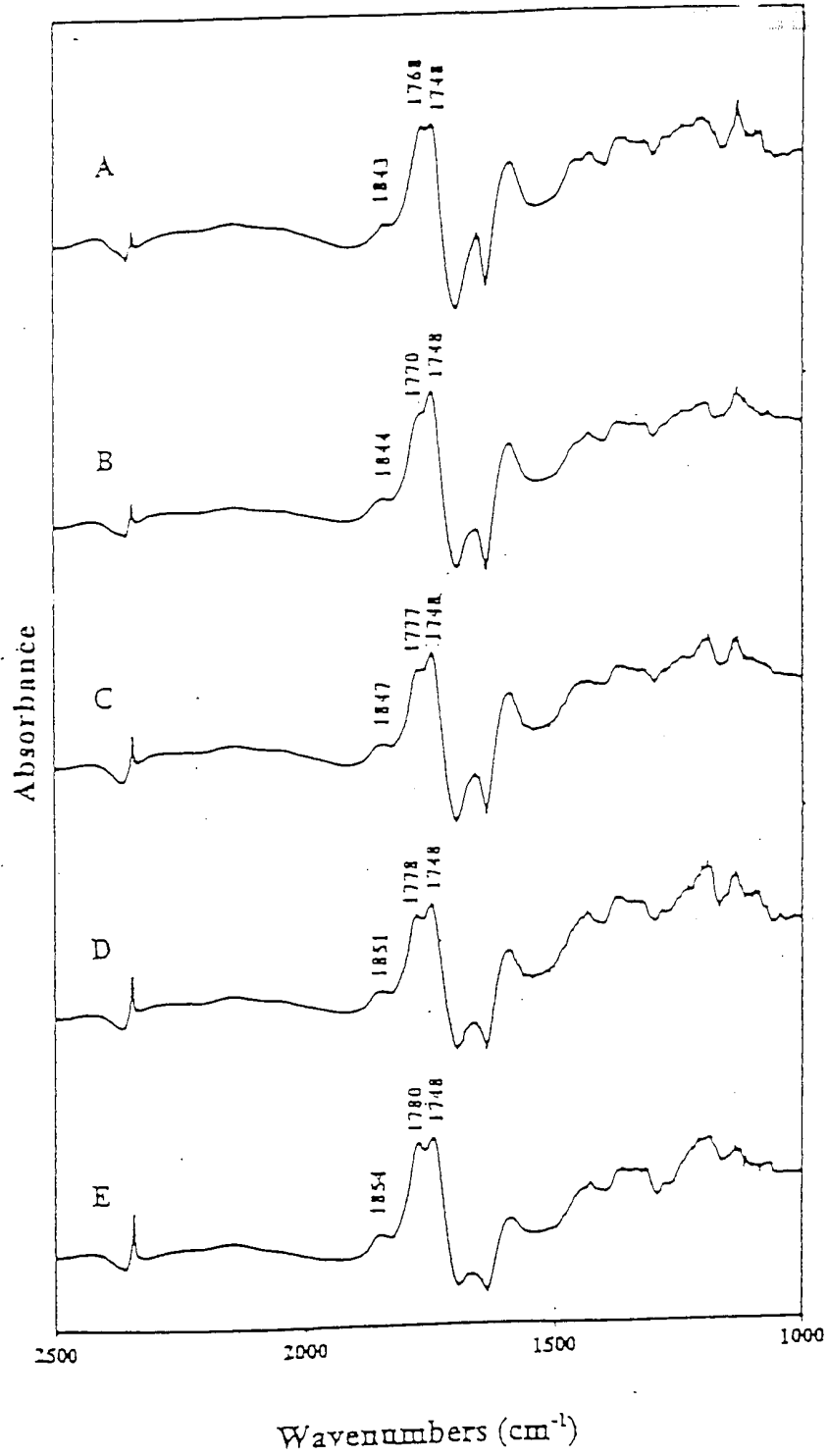


Figure 11

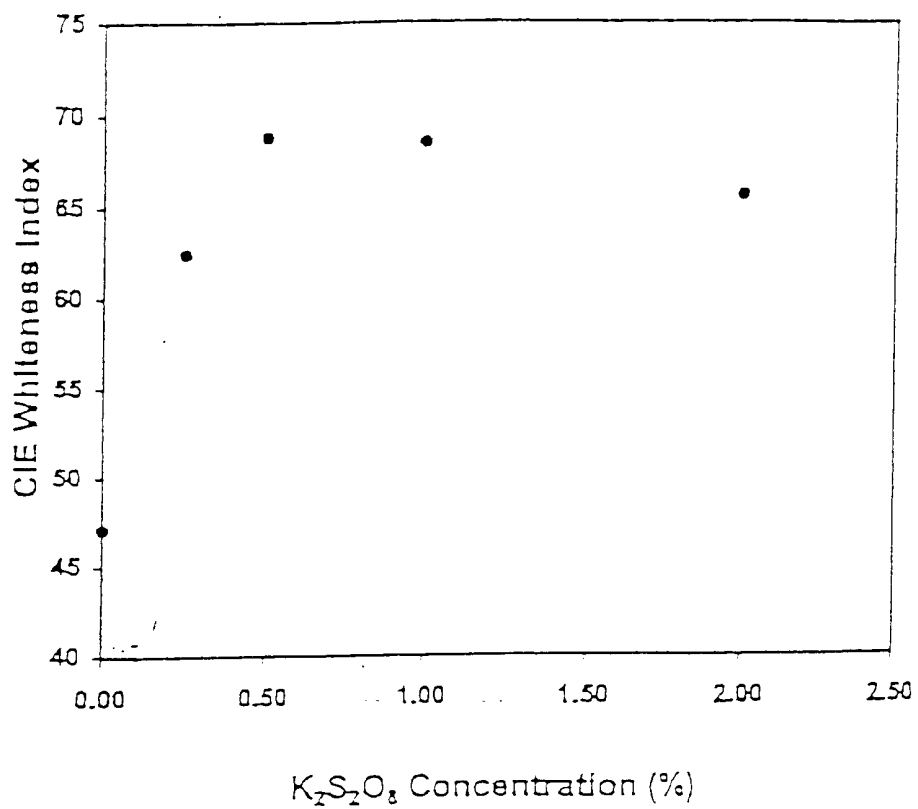


Figure 12

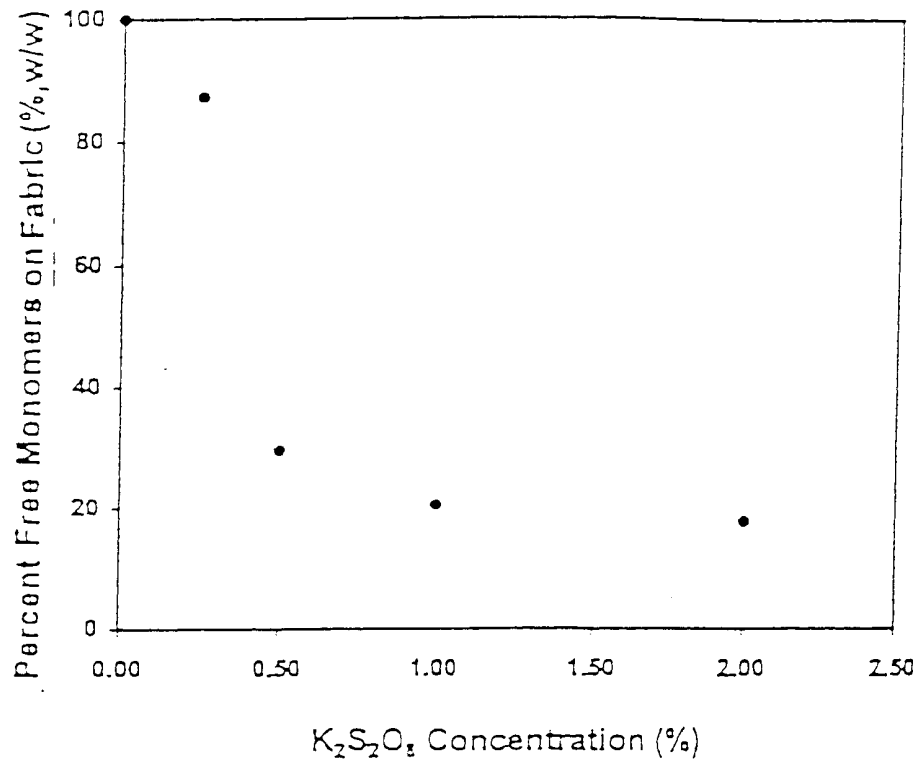


Figure 13

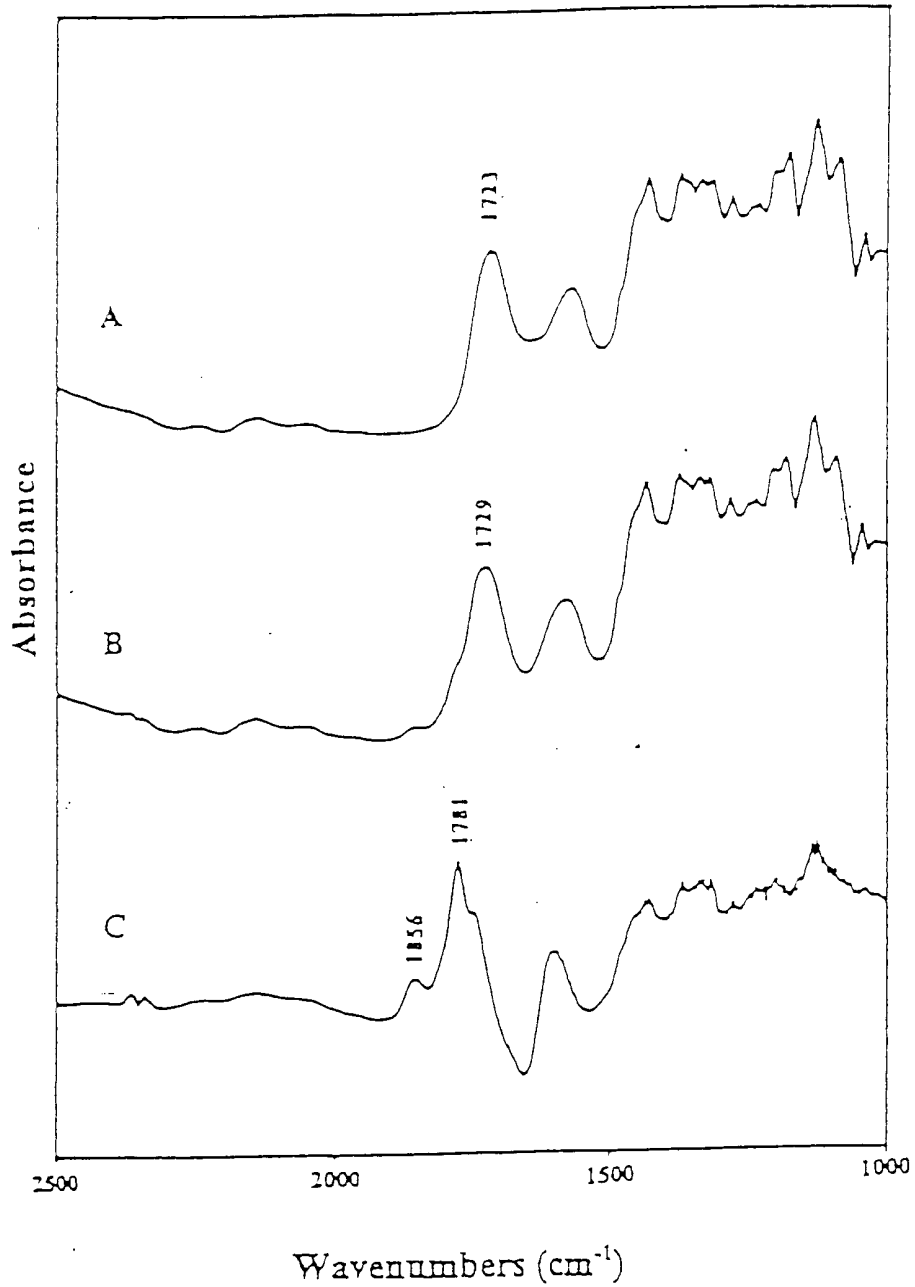


Figure 14

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/40990**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C08F 22/02, 2/16, 20/04

US CL : 526/318.2; 318.4, 90, 230, 234, 307.70, 271, 272.91

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/318.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0; CAS ONLINE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 5,336,744 A (SWIFT et al) 09 August 1994, abstract, col.3, lines 13-31, lines 36-64, col.4, lines 4-19, examples I, II.	1-5, 10 ----- 6-9,20-26
Y	US 5,268,437 A (HOLY et al) 07 December 1993, abstract, col. 4, lines 35-40, col. 5, lines 1-6, 47-65, col. 6, lines 1-7, 41-42, 58-68, col. 7, lines 1-15, 66-68, col. 8, lines 1-6.	1-26
Y	US 4,709,091 A (FUKIMOTO et al) 24 November 1987, abstract, col. 1, lines 45-51, col.2, lines 1-26, col. 3, lines 44-55, examples 1, 2, claims 1-4, 5, 6.	1-7, 10, 20, 21, 23-26

 Further documents are listed in the continuation of Box C.
  See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 DECEMBER 2000

Date of mailing of the international search report

17 JAN 2001

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/40990

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,135,677 A (YAMAGUCHI et al) 04 August 1992, abstract, col.4, lines 6-20, col.5, lines 9-20, col.6, lines 32-38, col.7, lines 8-15, col.8, lines 25-31, examples 1-24.	1-11, 20, 21, 24, 26.
Y	US 3,869,432 A (GAYLORD) 04 March 1975, abstract, col.1, lines 54-60, col.2, lines 44-50, col.3 and 4, examples 1-13.	12-19
A	US 5,574,120 A (HEIDEL et al) 12 November 1996, entire document, especially abstract, col.3, lines 1-34, 49-51, col.4, lines 58-67, col.6, lines 5-10.	1-11, 20-26