Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Mehmet Mürşit Temüz[a]; Mehmet Coşkun[a]; Ali Ölçücü[a]
[a] Faculty of Science and Arts, Department of Chemistry, University of Fırat, Elazığ, Turkey

To cite this Article Temüz, Mehmet Mürşit , Coşkun, Mehmet and Ölçücü, Ali(2007) 'Synthesis of Graft Copolymers of Cellulose with 4-Acryloylmorpholine, 2-Methacrylamidopyridine and N-Phenylmethacrylamide, and Determination of Some Sorption Properties', Journal of Macromolecular Science, Part A, 44: 9, 947 — 952

To link to this Article: DOI: 10.1080/10601320701424214

URL: http://dx.doi.org/10.1080/10601320701424214

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 947–952

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320701424214

Synthesis of Graft Copolymers of Cellulose with 4-Acryloylmorpholine, 2-Methacrylamidopyridine and N-Phenylmethacrylamide, and Determination of Some Sorption Properties

MEHMET MÜRŞIT TEMÜZ, MEHMET COŞKUN, and ALI ÖLÇÜCÜ

Faculty of Science and Arts, Department of Chemistry, University of Fırat, Elazığ, Turkey

Received January, 2007, Accepted February, 2007

Some new cellulosic materials having water-and dye-uptake capacity and being suitable for the sorption of metal ions were synthesized by the grafting of cellulose with the amide monomers such as 4-acryloylmorpholine, 2-methacrylamidopyridine and N-phenylmethacrylamide. At first, cellulose methacrylate was prepared by esterification of primary -OH group with methacryloyl chloride with a 16.7% yield by mole. The amide monomers were grafted into cellulose methacrylate via free radical polymerization using α,α'-azobisisobutyronitrile (AIBN) as an initiator in acetonitrile. The graft copolymers were characterized by FT-IR spectra, elemental analyses and thermal analysis. Dye-uptake and dye-absorption properties of cellulose for alizarine yellow (basic dye) and bromocresol green (acidic dye), its moisture- and water-uptake capacities, and its metal ion sorption tendency (for Cu^{2+}, Co^{2+} and Zn^{2+}) improved with the grafting. A different behavior was observed for Ni^{2+} ion sorption.

Keywords: cellulose; graft copolymer; vinyl monomers; sorption properties

1 Introduction

Celluloses with high molecular weights are naturally occurring polymers which are used as clothing, housing and industrial products (1). Cellulose is very promising raw material available at low cost for the preparation of various functional polymers (2).

Grafting reactions provide a potential route for significantly altering the physical and the mechanical properties of a substrate polymer to specific end uses. Graft copolymerization of vinyl monomers onto cellulose fibers has been the subject of extensive studies since 1950. There has been intense research and development activity in the field since the early days (3), and a significant amount of literature refers to the graft copolymerization of vinyl monomers onto cellulose (4, 5). Potassium (mono)persulfate and ceric ions (2) are extensively used to form cellulose radicals directly in the graft copolymerization of vinyl monomers on cellulosic materials. Another method of grafting the cellulose is based on the preliminary reaction between OH cellulosic groups and (meth)acryloyl chloride to form cellulose with a certain number of cellulose with a monomeric double bond, and when vinyl monomers are polymerized by a suitable radical initiator, the grafted copolymer of cellulose and homopolymer are produced simultaneously, and the homopolymer is then separated by a suitable method (2). Atom transfer radical copolymerization is also a different method for the graft copolymerization of cellulose (2). As far as we know, there are very few studies related to this method in the literature.

A wide range of sorbents for metal ions (4), dye, moisture and water modifications of cellulose have been developed, and some of them have shown outstanding sorptive and uptake capacity (2). These properties of cellulose graft copolymers have been reported recently by many researchers (5–9).

In the present study, the primary OH groups in powder cellulose were first transformed to ester groups with methacryloyl chloride. This cellulose methacrylate was grafted with 4-acryloylmorpholine(AcM), 2-methacrylamidopyridine(MAP) and N-phenyl methacrylamide(PMA) which were obtained from the reaction of methacryloyl chloride with corresponding aromatic amines, in presence of 2,2′-azobisisobutyronitrile(AIBN) as an initiator in acetonitrile. Synthesized new graft

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Address correspondence to: Mehmet Coşkun, Faculty of Science and Arts, Department of Chemistry, University of Fırat, Elazığ 23119, Turkey. Fax: +90-0424-2330062; E-mail: mcoskun@firat.edu.tr

copolymers have shown such excellent properties as uptake-sorption of metal ions, dye, moisture and water.

2 Experimental

2.1 Materials

The purification of cellulose powder (Cell-OH) and the synthesis of MAP were reported in detail according to our previous works (2, 10). Methacryloyl chloride (Aldrich) and aniline (Fluka) were freshly distilled under vacuum prior to use. Potassium tert-butoxide, alizarin yellow (Aldrich), bromocresol green (Merck), metal salts [$Cu(CH_3COO)_2H_2O$, $Co(CH_3COO)_24H_2O$, $Ni(CH_3COO)_24H_2O$, $Zn(CH_3COO)_2$ $2H_2O$] (Merck) and all the other solvents were analytical grade, and were used as supplied.

2.2 Synthesis of N-phenyl Methacrylamide

Methacryloyl chloride (0.1 mol) in 20 mL dried tetrahydrofuran(THF) was added dropwise to a solution of aniline (0.2 mol) in 100 ml dried THF, over a 30 min period, at 0–5°C, and the contents of the reaction were stirred for an additional 1 h at the same temperature. Then, they were kept continuously stirred at room temperature (~20°C) for about 2 h. The reaction mixture was poured into an ice-water-HCl mixture. All of the mixture was kept at 4–5°C for about 72 h. The mixture was filtered, and then solid monomer was dried (Yield: 80%).

2.3 Synthesis of Cellulose Methacrylate

Cellulose methacrylate (Cell-MA) was prepared by a method adapted from the literature (2, 4). Cellulose powder (3.24 g) was swollen in acetonitrile (50 mL) at the room temperature overnight, and a solution of potassium-tert-butoxide (7.84 g) in acetonitrile (50 mL) was added into it. The reaction mixture was stirred at the room temperature for 4 h, and then methacryloyl chloride (0.2 mol) in acetonitrile (50 mL) was added dropwise with continuous stirring at the same temperature. The reaction mixture was refluxed for about 12 h, and then cooled and filtered. Cell-MA was washed with water, ethanol, acetone, and diethyl ether, and finally dried under vacuum.

2.4 Synthesis of Graft Copolymers

Graft copolymers were prepared by a method adapted from the literature (4). Cellulose methacrylate (1.0 g), amid monomer (5.0 g), acetonitrile (50 mL), and AIBN (0.05 g) were refluxed for 5 h under argon. Grafted copolymers were filtered and thoroughly washed with N,N-dimethylformamide, water, ethanol, acetonitrile, acetone, and diethyl ether to eliminate oligomers and homopolymers formed as byproducts in the reaction. The obtained graft copolymers were dried at 50°C under vacuum.

2.5 Metal Ions Sorption of Graft Copolymers

The metal ions sorption of the grafted copolymers was adapted from the literature (6–9). The stock solutions of the metal salts were prepared in distilled water. The concentration of the stock solution for each (Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) was 500 mg/L. A polymer sample(0.1 g), a stock solution(5 mL), and the sodium acetate-acetic acid buffer solution(10 mL) (pH = 6.2) were added to an Erlenmyer flask and diluted to 50 mL with distilled water, and then sealed. The mixture was stirred constantly at room temperature for 24 h. The mixture was filtered in order to eliminate the polymer, and the solution was diluted with distilled water, and the filtrate was analyzed for the amount of metal salts remaining after the sorption on the polymers. The different relationships used to express the sorption behavior are as follows (7, 11);

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in the feed}} \times 100$$

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of metal ion in the polymer} \times \text{Volume of solution (mL)}}{\text{Amount of metal ion left in the solution} \times \text{Weight of dry polymer (g)}}$$

$$\text{Retention capacity } (Q) = \frac{\text{Amount of metal ion in the polymer (mEq)}}{\text{Weight of dry polymer (g)}}$$

2.6 Dye Uptake and Dye Absorption of the Graft Copolymers

These properties were measured according to a method adapted from the literature (12). The relationship (calibration curve) between the absorbance and the dye concentration for each dye was first obtained from the absorbance measurements of various dye concentrations at 615 nm for an aqueous solution (pH 3.9) of bromocresol green or at 352 nm for that (pH 7.1) of alizarin yellow.

Graft copolymer (1 g) was placed in a 100 mL of bromocresol green solution (0.25 g dye in 1000 mL water) as an acidic dye, or of alizarin yellow solution (in the same concentration as the bromocresol green solution) as a basic dye, and the mixture was refluxed at 95°C for 2 h. The dye concentrations (C and C_o) were obtained by using the calibration curve from the absorbance of a dye bath measured after and before dying. Dye-uptake and dye-absorption values were calculated from the following equations:

$$\text{Dye-uptake } (\%) = \frac{C_o - C}{C_o} \times 100$$

$$\text{Dye-absorption (mg dye/g polymer)} = \frac{(C_o - C) \times V}{w}$$

where C_o and C are dye bath concentrations before and after dyeing, respectively, w is polymeric sample weight, and V is volume of the dye bath.

2.7 *Moisture and Water Uptake Properties of the Graft Copolymers*

These properties were measured according to a method adapted from the literature (12). A known amount (w_1) of each polymer, vacuum-dried, with particle size of 75–106 μm was put into a glass tube with a large bottom. For contact with saturated vapor of the polymers, these tubes were kept in a closed container containing water at 25°C for 24 h, and then weighed (w_2). Moisture-uptake (hygroscopicity) was calculated according to the following equation:

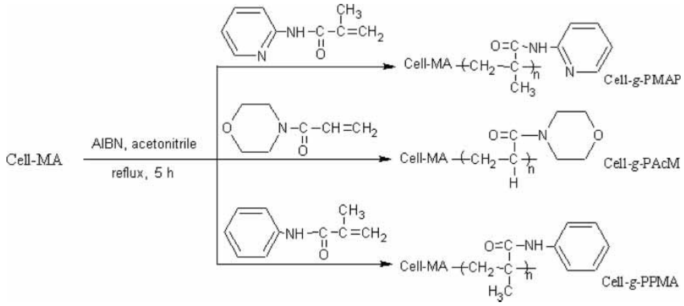
$$\text{Hygroscopicity } (\%) = \frac{w_2 - w_1}{w_1}$$

After the polymers used in hygroscopicity measurements had been dried thoroughly and weighed quickly (w_3), some water was added to each tube and kept at 25°C for 24 h, and then filtered, dried slightly with filter paper, and weighed (w_4). Water-uptake was calculated as follows:

$$\text{Water} - \text{uptake } (\%) = \frac{w_4 - w_3}{w_3}$$

2.8 *Characterization Techniques*

NMR spectra were recorded on a Jeol FX -90Q spectrometer. IR spectra were recorded with a Mattson 1000 FTIR spectrophotometer on solid samples as KBr pellets. Elemental analyses were carried out with a Leco 935 CHNS. Thermal analysis studies were performed on a Shimadzu TA-50 thermal analyzer. ATI UNICAM 929 Model atomic absorption spectrophotometer (AAS) was used for the metal ions determination.



Sch. 1. The grafting of cellulose with some amide monomers.

3 Results and Discussion

3.1 *Grafting of Cellulose and its Characterization*

The reaction of cellulose (Cell-OH) with potassium-*tert*-butoxide produces the alkoxide of cellulose only on primary OH group (2, 4), even if an excess amount of potassium-*tert*-butoxide was used. The treatment of the potassium cellulose alkoxide with methacryloyl chloride results in the formation of cellulose methacrylate (Cell-MA). As mentioned in the experimental section, a series of grafting studies on Cell-MA were carried out by using α,α'-azobisisobutyronitrile (AIBN) as a free radical initiator with 4-acryloylmorpholine (AcM), 2-methacrylamidopyridine (MAP), and N-phenyl methacrylamide (PMA) (Scheme 1). The graft copolymers were filtered and thoroughly washed with N,N-dimethylformamide, water, ethanol, acetonitrile, acetone, and diethyl ether to eliminate the oligomers and the homopolymers.

FT-IR (KBr) spectra of Cell-OH, Cell-MA, the graft copolymers of cellulose with poly(4-acryloylmorpholine) (Cell-*g*-PAcM), poly(2-methacrylamidopyridine) (Cell-*g*-PMAP), and poly(N-phenyl methacrylamide)(Cell-*g*-PPMA) are shown in Figure 1. The presence of a new band 1722 cm^{-1} (-C=O stretching), in which there is no band for Cell-OH, indicates that the methacrylate group has become attached to the cellulose. The C=C stretching vibration (~1635 cm^{-1}) in Cell-MA could not be observed due to the overlap of the O-H bending in the cellulose. The C=O stretching of amide group in the graft copolymers is a characteristic band. While this band is seen at 1637 cm^{-1} for Cell-*g*-PAcM, it is seen at 1660 cm^{-1} for Cell-*g*-PPMA and Cell-*g*-PMAP. The band at Cell-*g*-PAcM is relatively clearer.

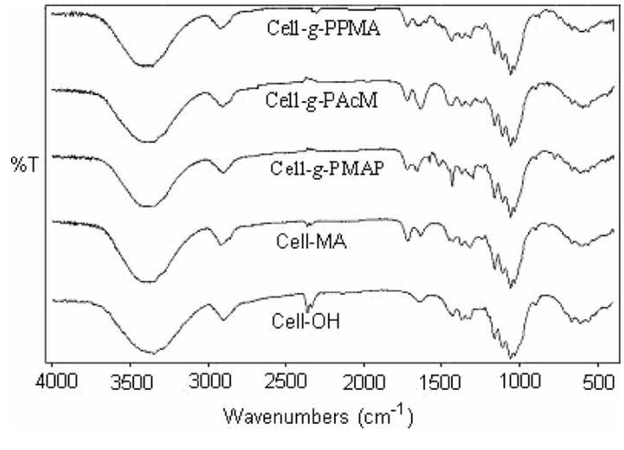
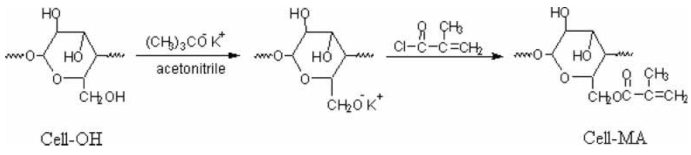


Fig. 1. FT-IR spectra of cellulose, cellulose methacrylate and the graft copolymers.



The elemental analyses of all the polymers are presented in Table 1. The substitution degree in the glucose units of cellulose was calculated as 16.7% by mole from the percentage of carbon as given in the literature (13). The levels of the grafting achieved at cellulose were expressed as the weight fraction of the corresponding amide monomers, and *x*- in each grafted polymer- was calculated by using the relationship (12):

$$E = (1 - x)A + \alpha x$$

Where A, E and α are the percentages of carbon by weight of substituted cellulose, the grafted cellulose and the monomer are used in the grafting, respectively. The ratio of the grafted vinyl segments to methacrylate groups in cellulose, n, was calculated by using the following relationship adapted from the literature (2):

$$n = \left(\frac{x/M_m}{(1 - x)/M_{av}}\right)(100/y)$$

Where M_m is the molar mass of the monomers, and M_{av} is the average molar mass of a cellulose unit obtained by using a substitution degree, the molar masses of Cell-MA and the unsubstituted cellulosic unit, y is the substitution degree in glucose units of cellulose (by mole). The *x* and *n* values calculated from the relationships above are shown in Table 1. It can be seen that the grafting degree of these amide based monomers on cellulose are relatively low (between 0.12–0.05 as weight fraction, *x*, and between 0.87–0.34 as the ratio of grafted vinyl segments to methacrylate groups in cellulose, *n*,).

The effect of grafting on the thermal stability of cellulose, as a part of characterization, was studied by using the thermogravimetric analysis (TGA) technique. The TGA curves of the grafted cellulose (Cell-*g*-PPMA, Cell-*g*-PMAP and Cell-*g*-PAcM) with the various amide monomers, Cell-MA and Cell-OH are represented in Figure 2. It has been seen that all the grafting processes and also the substitution have decreased the thermal stability of the original cellulose. While the initial decomposition temperature (IDT) of cellulose is about 290°C, those (270–220°C) of all the graft copolymers are lower than this value, including that of Cell-MA for which it is about 275°C. While 85% of cellulose decomposes between 350–390°C (a narrower temperature range), the others decompose over a wider range. While the graft copolymers left a residue between 11.5–17.2%, cellulose was 7% and Cell-MA was 8.3%. Similar thermal behavior has also been indicated in cases of cellulose grafted with methyl methacrylate, methacrylamide and acryloylmorpholine by atom transfer radical polymerization (2), methyl acrylate, methyl methacrylate and 2-hydroxyethyl methacrylate (14), cellulose partially esterified with some long-chain organic acids (15). This tendency has probably been related to some crosslinking reactions.

3.2 Dye Uptake and Dye Absorption of Graft Copolymers

Bromocresol green and alizarin yellow, which are acidic and basic dye, respectively, were employed to investigate the effect of grafting on the dyeability of the powder cellulose. The amount of the dye absorbed on Cell-OH, Cell-MA, Cell-*g*-PPMA, Cell-*g*-PMAP and Cell-*g*-PAcM was obtained by measuring dye-bath concentration before and after dyeing according to their light densities from the calibration curves. The results are shown in Table 2. The results clearly indicate that the substitution of cellulose with methacryloyl chloride and its grafting with PMA, MAP and AcM has improved greatly its dyeability.

In all polymers, it has been observed that the bromocresol green was absorbed more than the alizarin yellow. Two phenolic OH groups on bromocresol green molecules can easily associate with electronegative atoms on the repeating units of the grafted cellulose. In the case of alizarin yellow, whereas, one phenolic OH group cannot make strong intermolecular hydrogen bonding with cellulose and its derivatives including graft copolymers because of having a

Table 1. Elemental analyses and grafting of cellulose with some amid monomers

Polymer	C (%)	H (%)	N (%)	Weight fraction of amid monomer (*x*)	Ratio of amid segments to cellulosic units (*n*)
Cell-OH	42.66	5.81	—	—	—
Cell-MA	44.37	5.37	—	—	—
Cell-*g*-PMAP	46.97	5.44	2.07	0.12(0.131)[a]	0.87 (0.82)[b]
Cell-*g*-PAcM	45.58	5.60	0.76	0.08(0.095)[a]	0.64 (0.66)[b]
Cell-*g*-PPMA	46.02	5.40	0.45	0.05(0.056)[a]	0.34 (0.31)[b]

[a] Values in brackets were obtained from %N.
[b] Values in brackets were obtained by gravimetric analysis.

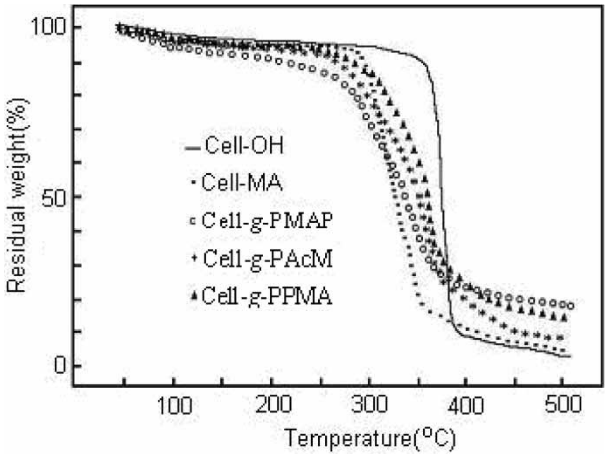
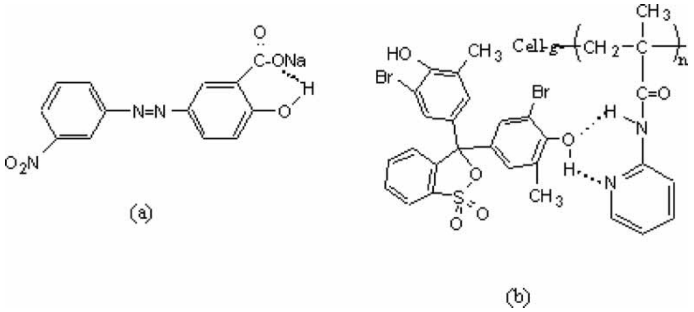


Fig. 2. TGA curves of cellulose, cellulose methacrylate and the graft copolymers.



Sch. 2. (a) Intramolecular hydrogen bonding in alizarin, (b) hydrogen bonding between bromocreso green and metharylamidopyridine units in Cell-g-PMAP.

suitable position to form an intramolecular hydrogen bonds (Scheme 2a). In comparison with each other (at Table 2), it is seen that Cell-*g*-PMAP has resulted in considerable higher dye-uptake and dye-absorption values than the others for both of the dyes, since the acidic dye (bromocresol green) can form strong hydrogen bonds with methacrylamidopyridine units in side-chain of Cell-*g*-PMAP (Scheme 2b). The basic dye (alizarin yellow) can also form strong hydrogen bonds with amidic hydrogens on methacrylamidopyridine units. N-phenyl methacrylamide units in Cell-*g*-PPMA can also associate with both of acidic and basic dyes through hydrogen bonding. Low grafting degree of Cell-g-PPMA has not increased the dye-uptake and the dye-absorption at the expected level. The high tendency in dye-uptake and dye-absorption of acidic dye on cellulose, Cell-MA and the graft copolymers are comparable with those of an acidic dye on AN-*g*-casein (12) and with those of bromocresol green on the graft copolymer of cellulose with methyl methacrylate, acryloylmorpholine and methacrylamide obtained by atom transfer radical polymerization (ATRP) (2). The results of the basic dye are somewhat lower than those obtained from the system of itaconic acid-*graft*-cellulose and two basic dyes (5), probably, because of the high effect of acid groups of itaconic acid on uptake of the basic dyes.

Table 2. Dyeabilities of the graft copolymers, powder cellulose and substituted cellulose

	Dye-uptake (%)		Dye-absorption (mg dye/g polymer)	
Polymer	Bromocresol green	Alizarin yellow	Bromocresol green	Alizarin yellow
Cell-OH	28.0	15.1	7.0	3.8
Cell-MA	47.6	27.3	11.9	6.8
Cell-*g*-PMAP	94.3	54.4	23.6	13.6
Cell-*g*-PAcM	70.5	42.7	17.6	10.7
Cell-*g*-PPMA	54.2	33.5	13.5	8.4

The grafting of cellulose with acrylomorpholine was carried out by ATRP in Reference 2 by free radical polymerization in this study, and the grating degrees as ratio of amid(-vinyl) segments to cellulosic units(n) were 2.61 and 0.64, respectively. The comparison indicated that dye-uptake and dye-absorption values of the graft copolymer obtained from ATRP were some higher than those of obtained in this study because of the ratio of the amid(vinyl) segments to cellulosic units(n).

3.3 *Moisture- and Water Uptake of Graft Copolymers*

The results given on moisture- and water uptake in Table 3 show that the grafting of cellulose with MAP, AcM and PMA has caused this capacity to increase considerably more than others in case of MAP. Water is able to form hydrogen bonds with amide groups in side-chain of all the graft copolymers, and this causes solubility tendency in the water of the graft copolymers to increase. It has been reported that the grafting of cellulose with various mixture of methyl methacrylate and vinyl acetate (16), and with methyl methacrylate, acrylomorpholine and methacrylamide (2) has increased water uptake capacity.

3.4 *Metal Ion Sorption of the Graft Copolymers*

The results of the study on metal ion (Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) sorption behaviors of the graft copolymers

Table 3. Moisture and water uptake values of the polymers

Polymer	Moisture-uptake (%)	Water-uptake (%)
Cell-OH	34.3	376.6
Cell-MA	59.7	503.1
Cell-*g*-PMAP	85.2	954.5
Cell-*g*-PAcM	66.5	736.8
Cell-*g*-PPMA	61.3	532.4

Table 4. Sorption behavior of cellulose, substituted cellulose, and its graft copolymers towards metal ions

	Cu^{2+}			Co^{2+}			Ni^{2+}			Zn^{2+}		
Polymer	P_u	K_d	Q	P_u	K_d	Q	P_u	K_d	Q	P_u	K_d	Q
Cell-OH	22.0	141.03	0.17	22.0	141.03	0.16	25.2	168.45	0.18	16.4	98.09	0.13
Cell-MA	10.8	60.54	0.09	10.8	60.54	0.08	20.8	131.31	0.15	11.6	65.61	0.09
Cell-*g*-PMAP	26.4	179.35	0.21	27.2	186.81	0.20	22.8	147.67	0.17	17.6	106.80	0.14
Cell-*g*-PAcM	12.8	73.39	0.10	23.6	154.45	0.17	18.8	115.76	0.14	15.6	92.42	0.13
Cell-*g*-PPMA	21.2	134.52	0.17	18.8	115.76	0.14	14.4	84.11	0.11	14.0	81.40	0.11

(Cell-*g*-PMAP, Cell-*g*-PAcM and Cell-*g*-PPMA) are summarized at Table 4. Metal ions are partitioned between the swollen polymer and the liquid phase, and they are reflected in high values of partition coefficients (K_d). All sorption values of the cellulose substituted for methacryloyl chloride (Cell-MA) are lower than those of Cell-OH and of all the graft copolymers (Cell-*g*-PMAP, Cell-*g*-PAcM and Cell-*g*-PPMA). Amid groups in the graft copolymers and hydroxyl groups in cellulose interact more easily with water as compared with methacrylate groups bonded cellulose, and this means that Cell-MA swells in water less than the others, and that metal ions penetrate into Cell-MA less than the others. Sorption values of Cell-*g*-PMAP, for all metal ions except Ni^{2+}, are higher than those of Cell-OH, Cell-MA and the other copolymers. The compounds having aminopyridine ring are widely used as binding materials for some transition metal ions such as Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ru^{3+} (17–20). Sorption values on Cell-OH of Ni^{2+} are 25.2, 168.45 and 0.18 as percent uptake (Pu), partition coefficient (K_d) and retention capacity (Q), respectively, and these values are higher than those of all the graft copolymers, and this means that OH groups on cellulose.

4 Conclusions

In this study, cellulose methacrylate was first prepared by esterification of primary –OH group with methacryloyl chloride with a 16.7% yield by mole.The amide monomers such as 4-acryloylmorpholine, 2-methacrylamidopyridine and N-phenylmethacrylamide, were grafted into the cellulose methacrylate via free radical polymerization using α,α'-azobisisobutyronitrile (AIBN) as an initiator in acetonitrile. The graft copolymers were characterized by FT-IR spectra, elemental analyses and thermal analysis.

The dye-uptake and dye-absorption properties of cellulose, for alizarine yellow (basic dye) and bromocresol green (acidic dye), and its moisture- and water-uptake capacities, increased between twice and four times with the grafting, and its metal ion sorption tendency (for Cu^{2+}, Co^{2+} and Zn^{2+}) improved with the grafting.

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