CELLULOSE CHEMISTRY AND TECHNOLOGY

CHARACTERIZATION AND MONOMER REACTIVITY RATIOS OF GRAFTED CELLULOSE WITH N-(4-NITROPHENYL)ACRYLAMIDE AND METHYL METHACRYLATE BY ATOM TRANSFER RADICAL POLYMERIZATION

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N-(4-nitrophenyl)acrylamide (4NPA) original monomer was synthesized and characterized by FT-IR, ^{1}H and ^{13}C NMR techniques. The atom transfer radical polymerization (ATRP) of 4NPA with methyl methacrylate (MMA) were performed in dimethylformamide (DMF) at 130 ^{0}C in the presence of cellulose chloroacetate (Cell.ClAc) macro initiator, Cu(I)Cl/2,2'-bipyridine catalytic system. The graft copolymers were characterized by elemental analysis, FT-IR spectra and thermal analysis. Thermal stabilities of the graft copolymers were determined by the TGA method and it was established that thermal stability of the copolymers increased with the increase of MMA units, while it decreased with the increase of 4NPA units. In order to investigate the effect of 4NPA with MMA monomer interactions on grafting, the graft copolymerization was also studied using different feed compositions, ranging from 0.15 to 0.85. The reactivity ratios of 4NPA and MMA by ATRP on cellulose were determined using the Finemann–Ross (F–R), inverted Finemann–Ross (inverted F–R), Yezrielev–Brokhina–Roskin (Y–B–R), Kelen–Tüdos (K–T) and extended Kelen–Tüdos (extended K–T) linearization methods. The reactive ratios of r_1 and r_2 were found to be 0.017-0.116 and 1.209-1.472, respectively. The graft copolymers on cellulose $r_1.r_2$ are close to zero.

Keywords: ATRP, cellulose, graft copolymer, monomer reactivity ratios

INTRODUCTION

Cellulose is a naturally occurring polysaccharide and the properties of cellulose may be modified suitably through graft copolymerization of different vinyl monomers. There is a considerable number of studies on grafting of individual vinyl monomers on cellulose, but very few reports are available on grafting on cellulose from a binary mixture of monomers. The technique of grafting from the binary mixtures of vinyl monomers of different functionalities facilitates the formation of graft copolymers with tailor-made properties for specific applications.[1] Very few reports are available about grafting of vinyl monomers from their mixtures onto cellulose.

Monomer reactivity ratios are important quantitative values for predicting the copolymer composition for any feed in any copolymerization. The concept of living free-radical copolymerization, such as ATRP, has attracted considerable interest because of the accurate control over the molecular weight and chain-end, the macromolecular architecture afforded by this technique, and no formation or very small amounts of individual homopolymers. Recently, copolymerizations via the ATRP procedure of some monomers have been studied, and their reactivity ratios have been determined.[2-7] K. C. Gupta and K. Khandekar carried out graft copolymerization of acrylamide-methylacrylate and acrylamide-methylmethacrylate comonomers, using ceric ammonium nitrate as initiator in the presence of nitric acid at 25 °C, and measured the effects of feed molarity, feed composition, reaction time and temperature on graft yield (%G) and other grafting parameters and, finally, reactivity ratios, with the Mayo-Lewis method.[8,9] K. C. Gupta and S. Sahoo reported in the 2000s on cellulose with acrylonitrile, on methylacrylate, ethylmethacrylate and methylmethacrylate graft copolymer mixtures, in an acidic environment with Ce(IV) ion initiator and measured reactivity ratios with the Mayo-Lewis method.[1,10,11]

Controlled/living vinyl addition polymerization giving a wide range of polymer structures is continuing to receive widespread attention.[12] It allows the controlled synthesis of a range of polymeric structures, such as block copolymers, graft copolymers, functional polymers and star polymers. In comparison with other controlled radical polymerization processes, atom transfer radical polymerization (ATRP)[13] is mechanistically more complex. ATRP utilizes a transition metal, e.g., Cu/bipyridine complex, as a halogen atom transfer reagent between the dormant and the active polymer chains with the rate constants of activation and deactivation, respectively. Thus, the catalyst reactivity depends on the ligand, the transition metal itself, and the initiating organic halide.[14,15] So far, copper-based systems seem to be the most efficient when compared to the other transition metals, such as iron, nickel, ruthenium and rhodium. The counter ions are often chloride and bromide, bromide normally yielding higher rates.[2,7]

This study aims at improving the grafting of cellulose by ATRP and describes the determination of the monomer reactivity ratios in the grafting of cellulose with 4NPA and MMA by ATRP. Some linear methods, such as the Finemann–Ross (F–R), inverted Finemann–Ross (inverted F–R), Yezrielev–Brokhina–Roskin (Y–B–R), Kelen–Tüdos (K–T) and extended Kelen–Tüdos (extended K–T) methods, were used for this purpose. Especially in grafting of insoluble cellulose, the ATRP method for the calculation of monomer reactivity ratios has been suggested to be one of the best methods. As the homopolymer was not obtained, the monomer concentration was constant for a long time.[2,16]

EXPERIMENTAL

Materials

4-Nitroaniline (Aldrich), chloroform, triethylamine [$(Et)_3N$] (Aldrich) were used as received. Tetrahydrofuran (THF) was dried on anhydrous $MgSO_4$ and freshly distilled prior to use. Acryloyl chloride (Aldrich) was freshly distilled under vacuum prior to use. Cellulose powder was supplied by Aldrich and was washed with dilute NaOH, water, dilute acetic acid, methanol, and acetone, and then dried under vacuum. Cuprous(I)chloride (Sigma), was used as received. Methyl methacrylate (MMA) (Aldrich) was first washed with dilute NaOH solution to extract the polymerization inhibitor, then with pure water, afterwards, it was dried and distilled under vacuum before use. Cellulose chloroacetate (Cell.ClAc) macro-initiator was synthesized in our laboratory.

Synthesis of N-(4-nitrophenyl)acrylamide (4NPA)

Acryloyl chloride (12 mmol) in 30 ml dried THF was added dropwise to a solution of 10 mmol 4-nitro aniline and 10 mmol $(Et)_3N$ in 250 ml dried THF, over 1 h period at 0-5 °C and the reaction contents were stirred. Then at room temperature, they were kept continuously stirred for about 12 h. The precipitate was filtered off, THF removed by a rotary evaporator, the reaction mixture was poured into ice-water mixture and was recrystallized in chloroform (yield: 65%). The synthesis of monomer is shown in Scheme 1.

Graft copolymerizations of 4NPA with MMA onto cellulose by ATRP

Cell.ClAc was prepared by a method adapted from the literature.[16] The general procedure for the copolymerization of seven compositions of 4NPA with MMA (A – G), varying from 0.85 to 0.15 by mole, is described below. In all cases, predetermined amounts of monomers, Cell.ClAc as macro-initiator, 2,2'-bipyridine as ligand and the calculated amount of CuCl as catalyst were added to a flask. The mixture was first degassed three times, stirred for 24 h in an oil bath and was heated to the required temperature, at 130 °C. After the mixture was cooled and filtered, it was washed with DMF, acetonitrile, chloroform, a mixture of water-ethanol-HCl, water, acetone and diethyl ether to eliminate oligomers and homopolymers formed as by-products in the reaction and, finally, the obtained graft copolymers were dried under vacuum.

The conversion of graft copolymerization was under 15%.

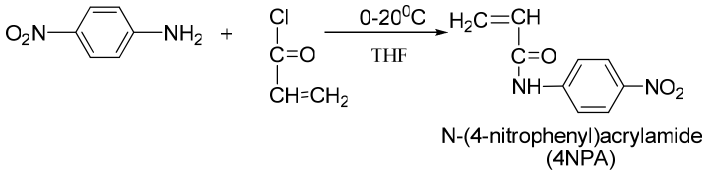
Instrumental measurements

NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature in DMSO-d_6. IR spectra were obtained with a Perkin Elmer Spectrum One FT-IR spectrophotometer on solid samples as KBr pellets. Thermal analysis was performed with a Shimadzu TGA-50 thermobalance at a heating rate of 10 °C min^{-1} in a nitrogen flow of 10 ml min^{-1}. Leco CHNS-932 was used for elemental analysis.

RESULTS AND DISCUSSION

Characterization of 4NPA

The chemical structure of 4NPA is shown in Scheme 1. ^1H, ^{13}C NMR and IR spectra of the monomer are indicated in Figs. 1 and 2. IR (cm^{-1}, the most characteristic bands): 1670 (C=O amide stretch), 1640 (C=C olefinic stretch), 3280 stretch and 1596 bending vibration (N–H), 1615 (C=C stretch on aromatic ring), 1500 asymmetric and 1344 symmetric stretch (NO_2). In the ^{1}H-NMR spectrum of the monomer, the following peaks appear: at 10.8 ppm for N-H, 8.2 and 7.9 ppm aromatic ring protons, 6.5 ppm for =CH olefinic, 6.3 and 5.9 ppm for $H_2C=$ olefinic protons. In the ^{13}C-NMR spectrum of the monomer, the following peaks appear: at 164 ppm for C=O, 147 ppm for C-NH, 143 ppm for C-NO_2, 131 ppm for =CH olefinic, 119 and 125 ppm for aromatic ring carbons and 127 ppm for CH_2.



Scheme 1: Synthesis of 4NPA monomer

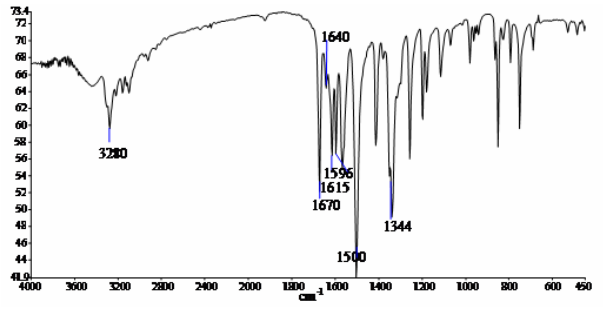


Figure 1: IR spectrum of original 4NPA monomer

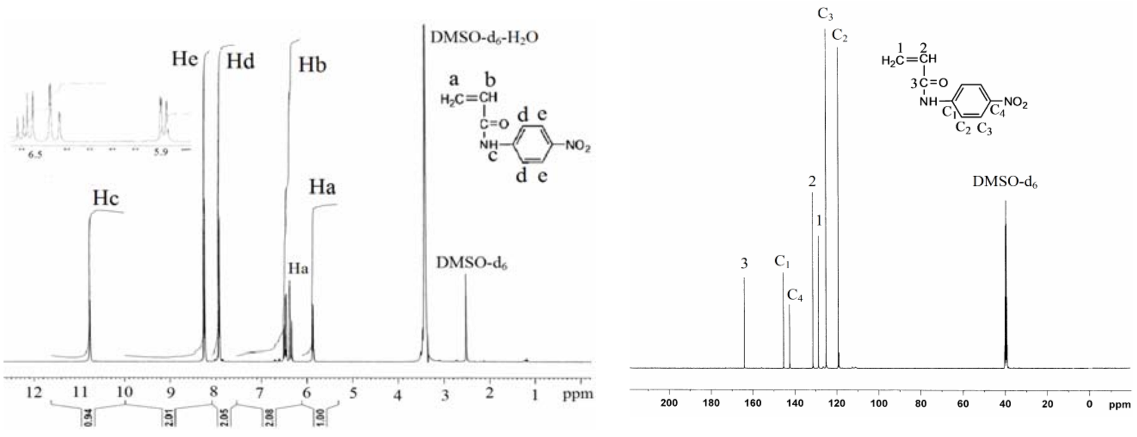
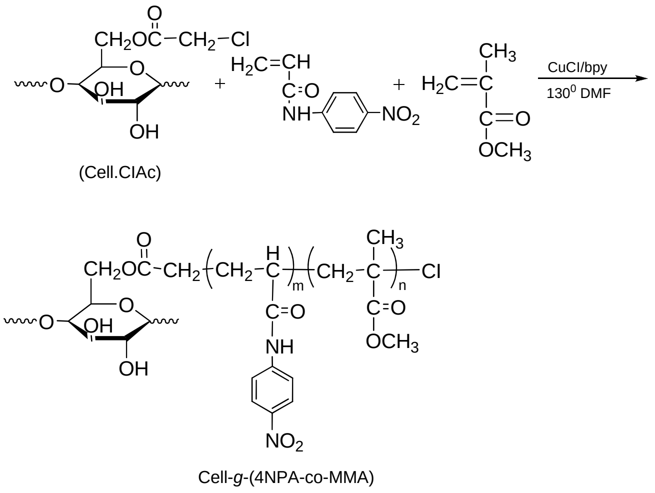


Figure 2: NMR spectra of 4NPA monomer

Synthesis and characterization of graft copolymers

The monomer reactivity ratios for the copolymerization of graft copolymers with 4NPA and MMA were determined from the copolymer composition. Graft copolymers Cell.ClAc/CuCl/ 2,2'-bipyridine/monomer mixture (mole 1:1:3:60) were prepared and added to a polymerization tube and then stirred under argon for about 1 h. The synthesis of the serials Cell-*g*-(4NPA-*co*-MMA) is indicated in Scheme 2. The IR spectra for the graft copolymers are presented in Figure 3. The IR spectra of Cell-*g*-(4NPA-*co*-MMA) show that, as the 4NPA content decreases in the graft copolymer, the amide carbonyl peak sharpness (band at 1670 cm^{-1}) decreases too, and the 1745 cm^{-1} ester band sharpness increases with MMA content. Also, the 1745 cm^{-1} ester band in the Cell.ClAc macro-initiator is observed for each graft copolymer.



Scheme 2: Synthesis of serial Cell-*g*-(4NPA-*co*-MMA)

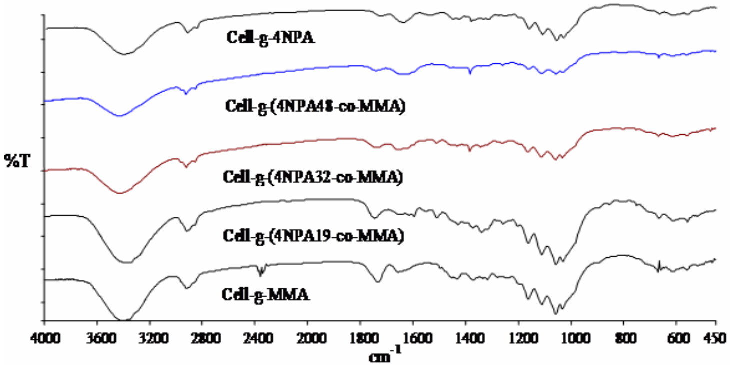


Figure 3: IR spectra of graft copolymers

Table 1
Elemental analysis, mole fraction of monomer in feed and in graft copolymers for Cell-g-(4NPA-*co*-MMA)

Graft copolymers	Elemental analysis			Mole fraction of 4NPA monomer in feed	Mole fraction of 4NPA monomer in graft copolymers*
	%C	%H	%N	4NPA (M_1)	4NPA (m_1)
A	43.90	6.03	4.51	0.85	0.55
B	43.02	6.44	4.00	0.70	0.48
C	43.62	5.71	3.73	0.60	0.44
D	43.89	6.51	2.77	0.50	0.32
E	44.04	7.01	2.00	0.40	0.22
F	45.07	6.43	1.70	0.30	0.19
G	45.58	6.05	1.01	0.15	0.11

* Calculated from nitrogen results in the graft copolymers

Calculation of monomer reactivity ratios of graft copolymerizations onto cellulose via ATRP

Table 1 shows the influence of the molar fraction of 4NPA in the graft copolymer (m_1), mole fraction of 4NPA monomer in feed (M_1) and nitrogen results of elemental analysis of 4NPA and MMA comonomers depending on the copolymer composition in ATRP. The substitution degree (%) in glucose units of cellulose was calculated as y = 36.5% by mole from the percentage of carbon as given in the literature.[16,17] This result showed that the substitution on the groups $-CH_2OH$ in cellulose was achieved to a high degree. So, Cell.ClAc average molecules weight was calculated for a unit:

$\bar{M} = y \cdot M_{Cell.ClAc} + (1- y) \cdot M_{Cellulose} = 189.9$

$2x14g\ N.m_1 / [189.9 + M_{4NFAA}.m_1 + M_{MMA}.(1- m_1)]$ = Elemental analysis indicated the value of N/100

The monomer reactivity ratios were obtained by the Finemann–Ross method (FR), the Inverted Finemann–Ross method (inverted F–R), the Kelen–Tüdos method (K–T), Yezrielev–Brokhina–Roskin (Y–B–R) and extended Kelen–Tüdos (extended K–T). The different parameters for the F–R, Invert F–R, K–T and Y–B–R methods are shown in Table 2; Table 3 summarizes the different parameters for the extended K–T method.

Table 2
Relative reactivity for Cell-*g*-(4NPA-*co*-MMA) in ATRP

Graft copolymers	$F=\frac{M_1}{M_2}$	$f=\frac{m_1}{m_2}$	$G=\frac{F(f-1)}{f}$	$H=\frac{F^2}{f}$	$\eta=\frac{G}{\alpha+H}$	$\xi=\frac{H}{\alpha+H}$	G/H	1/H	$H^{3/2}$
A	5.667	1.222	1.030	26.281	0.036	0.911	0.039	0.038	134.730
B	2.333	0.923	-0.195	5.897	-0.023	0.697	-0.033	0.170	14.320
C	1.500	0.666	-0.752	3.378	-0.127	0.569	-0.223	0.296	6.209
D	1.000	0.471	-1.123	2.123	-0.240	0.453	-0.529	0.471	3.093
E	0.667	0.250	-2.001	1.780	-0.461	0.410	-1.124	0.562	2.375
F	0.429	0.235	-1.397	0.783	-0.418	0.234	-1.784	1.277	0.693
G	0.176	0.124	-1.243	0.250	-0.442	0.089	-4.972	4.000	0.125

$\alpha = \sqrt{H_{max}.H_{min}} = 2.563$

The F–R equation[18] linearized different copolymerizations as follows:

$G = r_1H - r_2$

where $G = F.(f - 1)/f$, $H = F/f$, $F = M_1/M_2$, $f = m_1/m_2$, and M_1 and m_1 are mole fractions of 4NPA in feed and in the graft copolymer, respectively. A plot of G versus H gives r_1 as the slope and r_2 as the intercept. The inverted F–R equation gives r_1 as the intercept and r_2 as the slope: $G/H = -r_2/H+r_1$.

The equation proposed by Yezrielev *et al*[19] (the Y–B–R method) is the following:

$G = H^{3/2}.r_1-r_2$

The slope of the plot of G versus $H^{3/2}$ gives r_1, and the intercept of the same plot gives $-r_2$.

Kelen and Tüdos[20,21] (the K–T method) suggested another equation, introducing the terms η, α and ξ:

$H = (r_1 + r_2/\alpha).\xi - r_2/\alpha$

where $\eta = G/(\alpha+H)$, $\xi = H.(\alpha+H)$ and $\alpha = (H_{min}H_{max})^{1/2}$. The intercepts at $\xi = 1$ and at $\xi = 0$ of the plot of η against ξ gives r_1 and r_2/α, respectively. H_{min} and H_{max} are the lowest and highest values of H, respectively.

The F–R, inverted F–R, Y–B–R, and K–T plots obtained from the data in Table 2 are given in Figure 5(a-d).

Table 3
Parameters for extended K–T method

Graft copolymers	Conversion (w)	$\xi_2=\frac{w(\mu+F)}{(\mu+f)}$	$\xi_1=\xi_2.\left(\frac{f}{F}\right)$	$Z=\frac{\log(1-\xi_1)}{\log(1-\xi_2)}$	$H=\frac{f}{Z^2}$	$G=\frac{f-1}{Z}$	$\eta=\frac{G}{\alpha+H}$	$\xi=\frac{H}{\alpha+H}$
A	0.022	0.078	0.017	0.211	27.448	1.052	0.035	0.913
B	0.024	0.047	0.019	0.399	5.798	-0.193	-0.023	0.688
C	0.027	0.046	0.020	0.429	3.619	-0.779	-0.125	0.580

D	0.033	0.051	0.024	0.464	2.188	-1.140	-0.237	0.455
E	0.039	0.060	0.022	0.360	1.929	-2.083	-0.457	0.424
F	0.041	0.052	0.028	0.532	0.830	-1.438	-0.416	0.240
G	0.044	0.048	0.034	0.703	0.251	-1.246	-0.433	0.087

$\alpha = \sqrt{H_{\max} . H_{\min}} = 2.625$

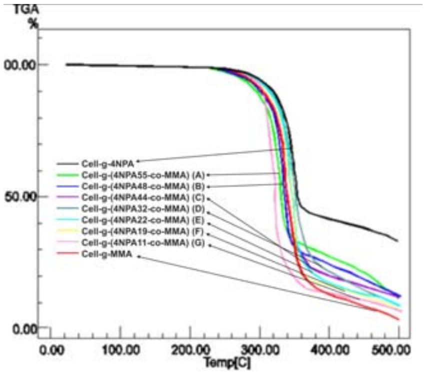
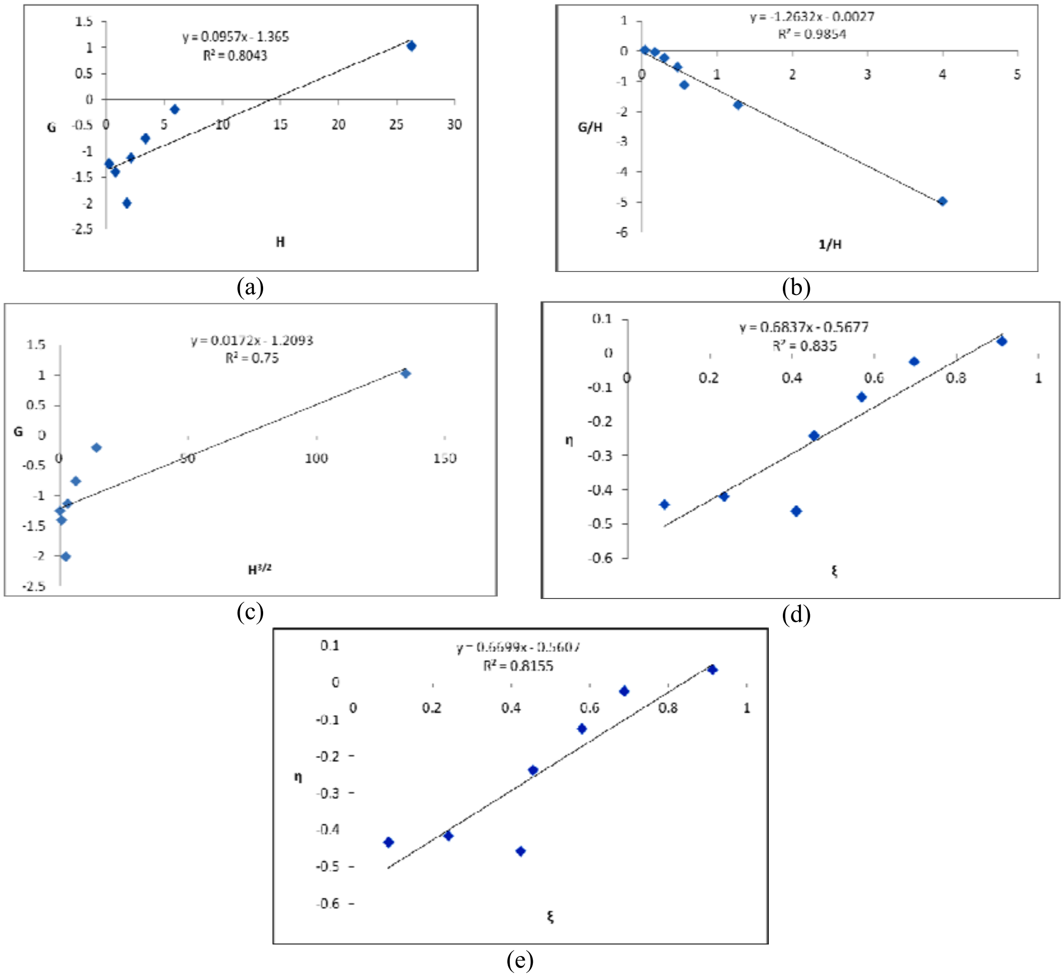


Figure 4: TGA curves of serial graft copolymers



(a)

(b)

(c)

(d)

(e)

Figure 5: (a) F–R plot, (b) inverted F–R plot, (c) Y-B–R plot, (d) K–T plot, (e) extended K–T plot

Kelen and Tüdos[21] improved their method one step further (extended K–T) to consider the effect of conversion on the polymer and comonomer compositions. For this purpose, parameters H and G were redefined as follows:
$H = f/Z^2$ and $G = (f - 1)/Z$, where $Z = \log(1-\xi_1)/\log(1-\xi_2)$. The partial molar conversions of 4NPA and MMA are defined as $\xi_2 = w.(\mu+F)/(\mu+f)$ and $\xi_1 = \xi_2.(f/F)$, respectively; w is the weight conversion of graft copolymerization on cellulose. An extended K–T plot is given in Figure 5(e).

From the slope and intercept of the straight line the r_1 and r_2 values calculated by various methods are summarized in Table 4. The results of the methods are in good agreement with each other.

Table 4
Comparison of monomer reactivity ratios by five methods

Methods	r_{4NPA}	r_{MMA}	$r_1.r_2$
FR	0.096	1.365	0.130
IFR	0.011	1.263	0.014
YBR	0.017	1.209	0.021
KT	0.116	1.455	0.169
EKT	0.109	1.472	0.160

Table 5
Thermal stabilities of graft copolymers with substituted cellulose

Polymers	(%) Initial decomposition temperature (°C)	Temperature of a wt loss of 50% (°C)	Residue, % at 500 °C
Cell-*g*-4NPA	220	355	29.9
A	222	353	20
B	226	351	15
C	230	350	13
D	235	350	9.9
E	239	349	9.9
F	243	346	8.5
G	247	343	8.9
Cell-*g*-MMA	250	340	8.7

Copolymer chains of cellulose, the grafts become richer in MMA units during the copolymerization. These results also suggest that MMA blocks may occur in the graft copolymer rich in MMA units.

Thermogravimetric study of graft copolymers

The thermogravimetric curves for Cell-*g*-4NPA, Cell-*g*-(4NPA-*co*-MMA) and Cell-*g*-MMA copolymers prepared by ATRP, which were obtained from room temperature to 500 °C at a heating rate of 10 °C/min under nitrogen flow, are given in Figure 4, as compared to with each other. It can be seen that the observed thermal stability of the copolymer increases with increasing MMA units in the graft copolymer system. Also, the amount of the residue in the graft copolymers decreased, while the MMA units were decreasing. The thermal behavior of a polymer depends on its structure and the type of substituents in the main chain. TGA results of the copolymers are summarized in Table 5.

CONCLUSION

4NPA original monomer was synthesized and characterized by IR, ^1H NMR and ^{13}C NMR spectroscopic techniques. 4NPA with MMA on cellulose was prepared by means of these groups using the Cell.ClAc/Cu(I)/2,2'-bipyridine complex as a catalyst in DMF at 130 °C, by ATRP. As it is expected, any homopolymer did not form during the grafting.[12-16] Graft copolymers were characterized by FT-IR, elemental analysis and termogravimetric analysis. Thermal stabilities were compared with each other and some others as thermogravimetric curves. The amount of the residue in the graft copolymers decreased, while the MMA unit decreased. This paper describes the determination of the monomer reactivity ratios in the grafting of cellulose with 4NPA and MMA by ATRP, with linear methods, such as the Finemann–Ross (F–R), inverted Finemann–Ross (inverted F–R), Yezrielev–Brokhina–Roskin (Y–B–R), Kelen–Tüdos (K–T) and extended Kelen–Tüdos (extended K–T) methods. The reactivity ratios of 4NPA and MMA in the graft copolymerization were found to be r_1 = 0.017-0.116 and r_2 = 1.209-1.472, with the various methods. According to the inverted F–R method, used in this study, the r_1 and r_2 values were found to be 0.011 and 1.263; $r_1.r_2$ = 0.014, respectively. The values calculated by all methods are very close. Two monomer mixtures on cellulose have a tendency to form an alternative copolymer, owing to the value of r_1, r_2 and $r_1.r_2$.

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