CELLULOSE CHEMISTRY AND TECHNOLOGY

MONOMER REACTIVITY RATIOS OF CELLULOSE GRAFTED WITH N-CYCLOHEXYLACRYLAMIDE AND METHYL METHACRYLATE BY ATOM TRANSFER RADICAL POLYMERIZATION

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The atom transfer radical polymerization (ATRP) of N-cyclohexylacrylamide (NCA) with methyl methacrylate (MMA) was performed in dimethylformamide (DMF) at 130 °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 found that the thermal stability of the copolymers increased with the increase of MMA units, while it decreased with the increase of NCA units. In order to investigate the effect of NCA interactions with MMA monomers on grafting, graft copolymerization was also studied using different feed compositions, ranging from 0.15 to 0.85. The reactivity ratios of NCA 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 obtained to be 0.004-0.128 and 0.657-0.907, respectively; $r_1.r_2$ of the graft copolymers on cellulose is close to zero.

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

INTRODUCTION

Cellulose is the most abundant natural polymer, which is used as raw or substituted in a number of applications, for instance in paper, packaging or lacquer technologies. Moreover, cellulose is biodegradable and obtainable from renewable sources, and thus, acceptable from the environmental point of view. However, to reach the required application properties, cellulose has to be modified, mostly by a reaction of hydroxyl groups leading to cellulose esters or ethers. In addition, cellulose backbone can be grafted with synthetic polymers via 'grafting from' or 'grafting onto' ways, using various polymerization techniques.[1] Thus, various materials were obtained by grafting, with many different properties, such as elasticity, ion exchange ability, thermal stability and mechanical properties. The grafting is mostly realized via free-radical polymerization initiated with redox systems, based prevailingly on ceric or ferrous salts or sodium hydrogen sulfite systems in combination with peroxides. Using these methods, a wide spectrum of cellulose–backbone graft copolymers with, e.g. acrylamide, methyl methacrylate, vinyl acetate or acrylonitrile grafts have been prepared; however, the number, density, length and molecular weight distribution of the grafts are virtually impossible to control. In addition to the vinyl monomers, heterocyclic lactones can be grafted from cellulose or its derivatives by ring-opening polymerization (ROP), giving in principle biodegradable polymeric materials.[2] Also, nitroxide mediated polymerization[3] or reversible addition–fragmentation chain transfer process (RAFT)[4] were recently applied to a controlled grafting of cellulose with synthetic polymers. In the recent years, a couple of papers have been published reporting on controlled cellulose grafting using ATRP.[5] First, the grafting can be performed in a heterogeneous system, i.e. on the surface of cellulose fibers or particles, giving surface-modified cellulose, which could be used, for instance, as filler in appropriate polymer composites.[6]

ATRP was discovered independently by Matyjaszewski *et al.* in 1995, and has ever since been widely used and studied, as it is a versatile tool for creating polymers with low polydispersity and controlled molecular weight.[6] Besides, ATRP is a useful method to synthesize graft copolymers with well-defined structures utilizing a variety of monomers. The application of ATRP to cellulose is a potentially attractive technique to prepare novel cellulose derivatives with well-defined side-chain structures. Despite the apparent utility of the technique, there are few reports on ATRP and the synthesis of cellulosic graft copolymers.[7-10] 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 due to 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.[9,10] Recently, copolymerization via the ATRP of some monomers has been studied, and their reactivity ratios have been determined. In the 2000's, K. C. Gupta and K. Khandekar carried out graft copolymerization of acrylamide-methyl-acrylate and acrylamide-methylmethacrylate comonomers on cellulose, using ceric ammonium nitrate as initiator, in the presence of nitric acid at 25 °C, and determined the effects of feed molarity, feed composition, reaction time, and temperature on graft yield (%G) and other grafting parameters. Also, they carried out graft copolymerization of binary mixtures of acrylonitrile-methylmethacrylate, acrylonitrile-ethylmethacrylate, and acrylonitrile-methylacrylate comonomers, using Ce(IV) ion as initiator, and determined the reactivity ratios by the Mayo-Lewis method.[11-15]

In order to improve the grafting of cellulose by ATRP, this study aims at determining the monomer reactivity ratios in the grafting of cellulose with NCA 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. Because the homopolymer was not obtained, the monomer concentration was constant for a long time.[9,10]

EXPERIMENTAL

Materials

Powdered cellulose, supplied by Aldrich, was washed with dilute NaOH, water, diluted 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, and with pure water, then evaporated from diethyl ether and dried under vacuum before use. Cell.ClAc as macro initiator and N-cyclohexylacrylamide (NCA) monomer were synthesized by a method adapted from the literature.[10,16-17]

Graft copolymerization of NCA with MMA onto cellulose by ATRP

The general procedure for the copolymerization of seven compositions of NCA with MMA (2-8), varying from 0.85 to 0.15 by mole, is described below. 1 and 9 indicate the graft copolymers of Cell-*g*-NCA and Cell-*g*-MMA. 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. Firstly, the mixture was degassed three times, stirred for 24 h, and was heated to the required temperature, at 130 °C. After, the mixture was cooled and filtered, it was washed with N, N-dimethylformamide, 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. Finally, the obtained graft copolymers were dried under vacuum. The conversion of the graft copolymerization was under 15%.

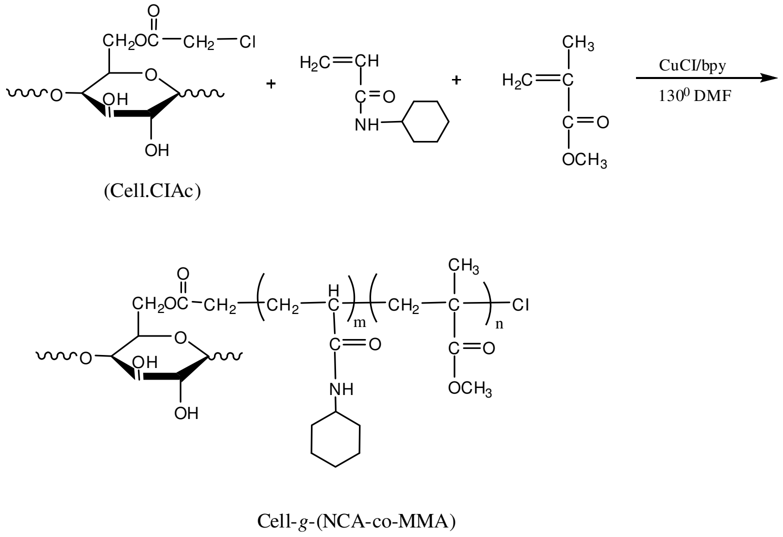
Instrumental measurements

FT-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}. Elemental analysis was carried out with Leco CHNS-932.

RESULTS AND DISCUSSION

Synthesis and characterization of graft copolymers

The monomer reactivity ratios for the copolymerization of graft copolymers with NCA 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, added to a polymerization tube and then stirred under argon for 15 min. The synthesis of the serials Cell-*g*-(NCA-*co*-MMA) is indicated in Scheme 1. The FT-IR spectra of the graft copolymers are presented in Figure 1. In the FT-IR spectra, the ester band of Cell.ClAc macro initiator at 1745 cm^{-1} is observed for each graft copolymer. Also, the FT-IR spectra of Cell-*g*-(NCA-*co*-MMA) show that as the NCA content decreases in the graft copolymer, the amide carbonyl peak sharpness (band at 1660 cm^{-1}) decreases too, and the 1745 cm^{-1} ester sharpness increases with MMA content.



Scheme 1: Synthesis of serial Cell-*g*-(NCA-*co*-MMA)

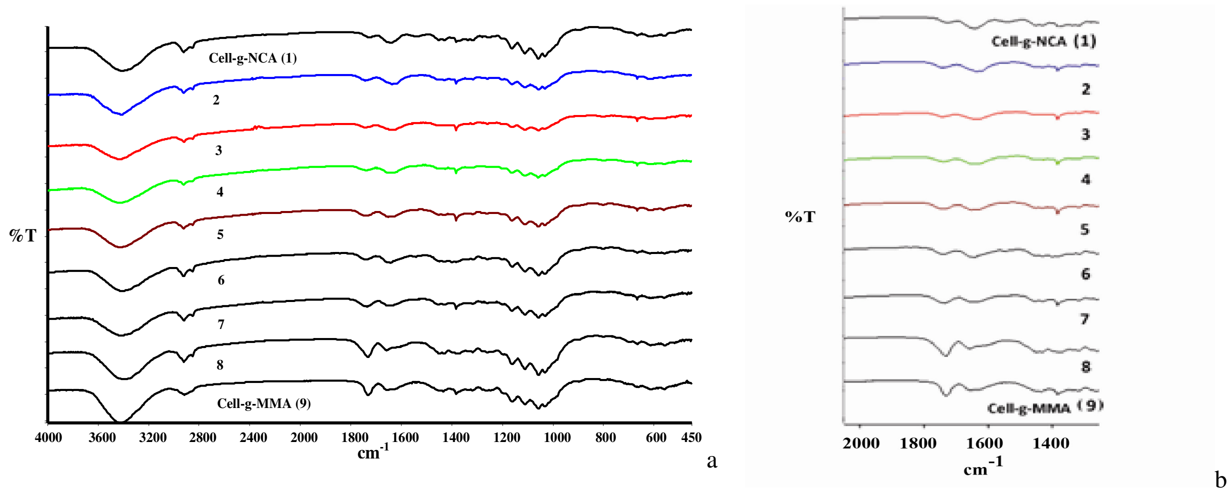


Figure 1: FT-IR spectra (a – 4000-450 cm^{-1}; b – 1400-2000 cm^{-1}) of graft copolymers

Calculation of monomer reactivity ratios of graft copolymerization

Table 1 shows the influence of the molar fraction of NCA in the graft copolymer (m_1), mole fraction of NCA monomer in feed (M_1) and nitrogen results of elemental analysis of NCA 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.[10,17-18] This result showed that the substitution of the primary –OH groups in cellulose was achieved to a great extent. So, Cell.ClAc molecule average weight was calculated for a unit:

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

14 g N.m_1 / [189.9 + M_{NCA}.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 (F–R), the Inverted Finemann–Ross method (Invert 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 1
Elemental analysis, mole fraction of monomer in feed and in graft copolymers for Cell-*g*-(NCA-*co*-MMA)

Graft copolymers	Elemental analysis			Mole fraction of NCA monomer in feed	Mole fraction of NCA monomer in graft copolymers*
	%C	%H	%N	NCA (M_1)	NCA (m_1)
2	43.90	6.03	2.16	0.85	0.498
3	43.02	6.44	2.11	0.70	0.485
4	43.62	5.71	1.87	0.60	0.425
5	43.89	6.51	1.65	0.50	0.370
6	44.04	7.01	1.40	0.40	0.310
7	45.07	6.43	1.23	0.30	0.270
8	45.58	6.05	0.66	0.15	0.141

* Calculated from nitrogen results in the graft copolymers

Table 2
Relative reactivity for Cell-*g*-(NCA-*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	$H^{3/2}$
2	5.667	0.992	-0.046	32.374	-0.001	0.929	-0.001	0.031	184.202
3	2.333	0.942	-0.144	5.778	-0.017	0.700	-0.025	0.173	13.889
4	1.500	0.739	-0.530	3.045	-0.096	0.552	-0.174	0.328	5.314
5	1.000	0.587	-0.704	1.704	-0.169	0.408	-0.413	0.587	2.224
6	0.667	0.449	-0.819	0.991	-0.236	0.286	-0.826	1.009	0.987
7	0.429	0.370	-0.731	0.497	-0.246	0.167	-1.471	2.012	0.350
8	0.176	0.164	-0.897	0.189	-0.337	0.071	-4.746	5.291	0.082

$\alpha=\sqrt{H_{\max}.H_{\min}}=2.474$

Table 3
Parameters for extended K-T method

Graft copolymers	Conversion (w)	$\xi_2=\frac{w(\mu+F)}{(\mu+f)}$	$\xi_1=\xi_2.\left(\frac{f}{F}\right)$	$Z=\frac{\log(1-\xi_1)}{\log(1-\xi_2)}$	$H=\frac{f}{Z^2}$	$G=\frac{f-1}{Z}$	$\eta=\frac{G}{\alpha+H}$	$\xi=\frac{H}{\alpha+H}$
2	0.027	0.106	0.019	0.171	33.925	-0.047	-0.001	0.930
3	0.030	0.057	0.023	0.404	5.772	-0.144	-0.017	0.695
4	0.032	0.050	0.025	0.494	3.028	-0.528	-0.095	0.544
5	0.034	0.046	0.027	0.581	1.739	-0.711	-0.166	0.406
6	0.037	0.045	0.030	0.662	1.025	-0.832	-0.233	0.288
7	0.039	0.041	0.035	0.851	0.511	-0.740	-0.243	0.168
8	0.043	0.044	0.041	0.930	0.190	-0.899	-0.329	0.070

$\alpha=\sqrt{H_{\max}.H_{\min}}=2.539$

The F–R equation[19,20] is linearized as the differential copolymerization equation in the following form: $G = r_1H - r_2$
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 NCA 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.*[21] (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[18,19] (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 from Figures 2 to 6.

Kelen and Tüdos 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 NCA 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 6.

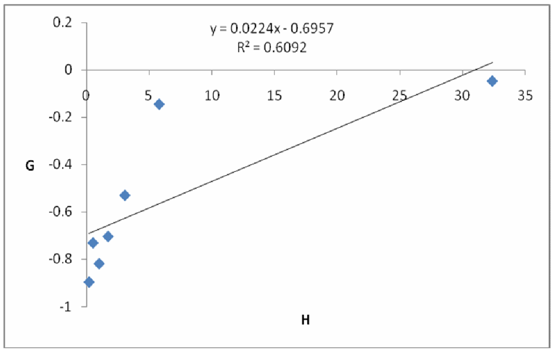


Figure 2: F–R plot

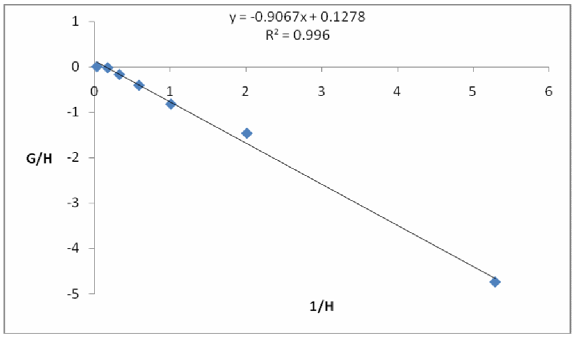


Figure 3: Inverted F–R plot

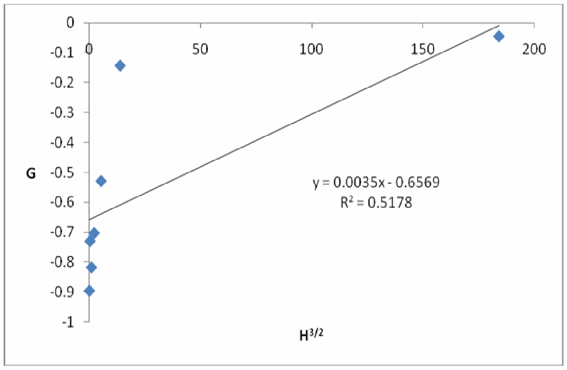


Figure 4: Y–B–R plot

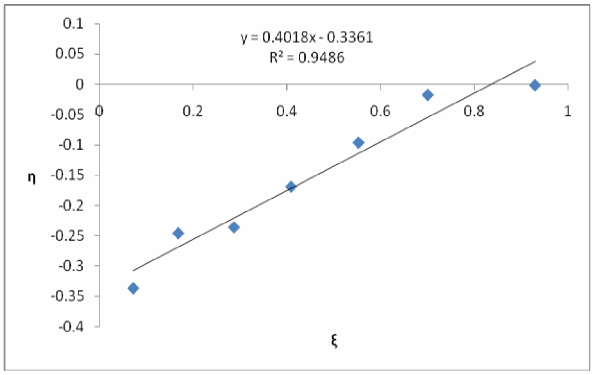


Figure 5: K–T plot

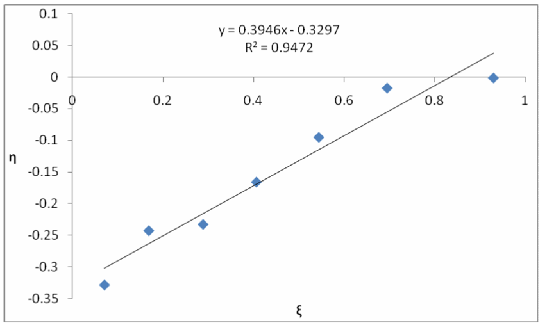


Figure 6: Extended K–T plot

Table 4
Comparison of monomer reactivity ratios by five methods

Methods	r_{NCA}	r_{MMA}	$r_1.r_2$
FR	0.022	0.696	0.015
IFR	0.128	0.907	0.116
YBR	0.004	0.657	0.003
KT	0.066	0.832	0.055
EKT	0.065	0.837	0.054
Average	0.057	0.786	0.049

Table 5
Thermal stabilities of graft copolymers with substituted cellulose

Polymer No	^aT_i (°C)	$^bT_{\%50}$ (°C)	%Weight loss at 400 °C	%Weight loss at 450 °C	Residue at 500 °C (%)
1	221	344	79	82	12.5
2	223	346	77	78	15
3	228	345	76	80	14
4	230	344	75	81	13
5	235	343	77	81	13
6	239	342	81	84	11.5
7	243	341	82	86	10.1
8	246	340	84	88	9.2
9	250	340	88	91	8.7

a: Initial decomposition temperature, b: Decomposition temperature at 50%

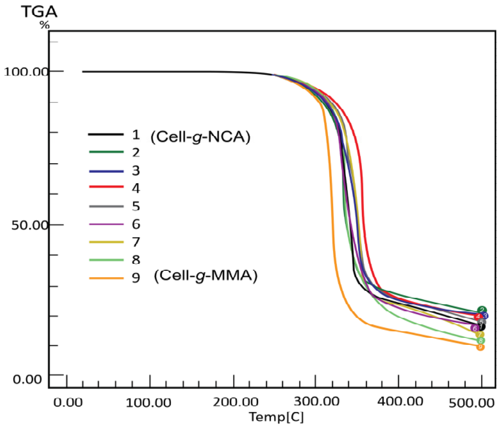


Figure 7: TGA curves of graft copolymers

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.

In the copolymer chains of cellulose, the grafts become richer in MMA units during the copolymerization. These results also suggest the possible presence of MMA blocks in the graft copolymer.

Thermogravimetric study

As a part of the characterization, the effect of grafting on the thermal stability of cellulose was studied by using the thermogravimetric analysis (TGA) technique. Figure 7 represents the TGA curves of the grafted celluloses Cell-*g*-NCA, series of Cell-*g*-(NCA-*co*-MMA) and Cell-*g*-MMA, if the initial decomposition temperature (IDT) and the temperature at 50% weight loss are taken as a measure of thermal stability. 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 decreased. The thermal behavior of a polymer depends on its structure and the type of the substituent in the main chain. TGA results of the copolymers are summarized in Table 5.

CONCLUSION

NCA monomer was synthesized and graft copolymers of this monomer with MMA on cellulose were prepared using the Cell.ClAc/Cu(I)/2,2'-bipyridine complex as catalyst in DMF, at 130 °C by ATRP. Graft copolymers were characterized by FT-IR, elemental analysis and thermogravimetric analysis. Thermal stabilities were compared considering the thermogravimetric curves. The amount of the residue in the graft copolymers decreased, while the MMA units decreased. Also, the monomer reactivity ratios in the grafting of cellulose with NCA and MMA by ATRP were determined by 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 NCA and MMA in the graft copolymerization were found to be $r_1 = 0.004$-0.128 and $r_2 = 0.657$-0.907 with the mentioned methods. The values calculated by all methods very close to them. Two monomer mixtures on cellulose have a tendency to form an alternating copolymer, because the value of r_1, r_2 and $r_1.r_2$ have approached zero.

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