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Controlled grafting of cellulose diacetate

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Abstract

Cellulose diacetate (CDA) was acylated with 2-bromoisobutyryl bromide (BriBr) or with dichloroacetyl chloride (ClAcCl) giving polyfunctional macroinitiators for ATRP grafting of styrene (St), MMA and butyl acrylate (BuA). Under various reaction conditions, macroinitiators with variable degrees of functionalisation could be prepared. The macroinitiators with 2-bromoisobutyryl (BriB) groups were grafted with St or BuA, those with dichloroacetyl (ClAc) functions were used for graft copolymerization of MMA. Graft copolymers with chemically different grafts as well as tunable lengths and densities of grafts were synthesized in this way. Poly(CDA-*g*-St) and poly(CDA-*g*-MMA) were further used as macroinitiators of BuA polymerization, giving poly[CDA-*g*-(St-*b*-BuA)] and poly[CDA-*g*-(MMA-*b*-BuA)] graft copolymers with diblock grafts.

Keywords: Cellulose diacetate; Functionalization; ATRP

1. Introduction

Atom transfer radical polymerization (ATRP) as a modern method of tailoring of polymers [1,2] offers a very wide spectrum of applications including modifications of known materials by grafting, because carbon halide-type active sites can be easily generated on various polymer chains. It was shown recently that the ATRP can be also applied to the modification of cellulose or its derivatives. Cellulose is the most abundant natural polymer, which is used as such or its derivatives in a number of applications, for instance in paper, packaging or lacquer technologies [3,4]. 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 hydroxy groups leading to cellulose esters or ethers [5,6]. In addition, cellulose backbone can be grafted with synthetic polymers via 'grafting-from' or 'grafting-onto' ways, using various polymerization techniques. 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 hydrogensulfite systems in combination with peroxides [7–9]. 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. Only a few papers have described cellulose grafting with uniform grafts using various methods. For instance, monodisperse carboxy-functionalized polystyrene, prepared by anionic polymerization, was transferred to acyl halide and reacted with the residual hydroxyl groups of cellulose acetate [10]. Further, cationically prepared 'living' poly(2-methyl-2-oxazoline) or poly(isobutyl vinyl ether) were terminated with cellulose, into which amino groups were introduced [11]; also here, more or less uniform grafts were obtained. In addition to the vinyl monomers, also heterocycles, such as lactones, can be surface grafted from cellulose or its derivatives by ring-opening polymerization (ROP), giving in principle biodegradable polymeric materials [12–14]. In addition, also nitroxide-mediated polymerization [15] or reversible addition–fragmentation chain transfer process (RAFT) [16] were recently also applied to a controlled grafting of cellulose with synthetic polymers.

In the recent years, a couple of papers have appeared reporting on controlled cellulose grafting using ATRP. First, the grafting can be performed in heterogeneous system, i.e. on the surface of cellulose fibers or particles, giving surface-modified cellulose,

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which could be used, for instance, as a filler in appropriate polymer composites [17,18]. Thus, cellulose fibers (filter paper) were in the first step surface-acylated with 2-bromoisobutyryl bromide [19], giving the fibers with chemically anchored initiating sites, which were subsequently used for ATRP grafting of methyl acrylate (MA). Further [20], these fibers with the anchored polyMA brush were used as macroinitiators of ATRP of 2-hydroxyethyl methacrylate (HEMA), leading to poly(MA-*b*-HEMA) surface anchored copolymers. In another work [21], cellulose powder was surface-acylated with chloroacetic acid chloride and the anchored chloroacetyl groups then used as initiating sites for ATRP grafting of styrene, MMA, methacrylamide or 4-acryloylmorpholine. Thermal stability, water or dye absorption of the obtained surface modified cellulose particles was studied. Similarly, cellulose was acylated with 2-chloropropanoyl halide and the product used for ATRP grafting copolymerization of MMA and styrene under CuBr/pentamethyldiethylenetriamine catalysis [22]. As well as cellulose particles, cellulose derivatives, (esters and ethers), can also be grafted in similar ways with vinyl or heterocyclic monomers; however, true graft copolymers are formed in this case. ATRP grafting of cellulose diacetate (CDA) with PMMA was recently presented by Shen and Huang [23], initiated with 2-bromoisobutyryl groups, introduced onto CDA chains by acylation reaction.

In this work we present grafting of CDA, functionalized with 2-bromoisobutyryl or dichloroacetyl groups as initiating sites for ATRP of styrene, MMA, butyl acrylate and some block copolymers.

2. Experimental

2.1. Materials

Cellulose acetate, (Fluka, molecular weight ca. 37,000), was analyzed by NMR; it was found that its degree of acetylation is approximately two. Before use, the powder was dried under vacuum at 50 °C and kept under argon. Styrene (St), methyl methacrylate (MMA) and butyl acrylate (BuA) (Fluka) were vacuum-distilled with calcium hydride and stored under argon atmosphere. 1,4-Dioxane and acetone were distilled with calcium hydride under argon atmosphere. 2-Bromoisobutyryl bromide, dichloroacetyl chloride, methyl dichloroacetate, 4-(dimethylamino)pyridine (DMAP) and triethylamine (TEA) (Fluka) were used as received. The catalyst components, i.e. CuCl, $CuCl_2$, Cu powder, hexamethyltriethylenetetramine (HMTETA), pentamethyldiethylenetriamine (PMDETA) and 2,2′-bipyridine (bPy) (Fluka) were also used without purification.

2.2. CDA functionalization

CDA was acylated either with 2-bromoisobutyryl bromide (BriB-Br) or with dichloroacetyl chloride (ClAc-Cl) in the presence of TEA and under DMAP catalysis at room temperature [24]. In the first case, acylation was performed in 1,4-dioxane, in the latter in acetone. The degree of functionalization was governed by an excess of acyl halide over CDA. Typically: 5 g of pre-dried CDA was dissolved in 50 ml of distilled acetone in a 100-ml flask with a magnetic stirring bar and 3.48 ml (25 mmol) of TEA and 2.48 g (20.3 mmol) of DMAP was added into solution. Then, the flask was cooled down to ca. 0 °C with ice-bath and 1.95 ml (20.3 mmol) of dichloroacetyl chloride was added dropwise under argon atmosphere. The reaction mixture was stirred at the same temperature for additional 1 h, then left to warm up to room temperature and mixed overnight. The salt was removed by filtration and the filtrate was diluted with 30 ml of acetone. The functionalized CDA was isolated by precipitation of the acetone solution into 20-fold excess of water, washed repeatedly with 1/1 methanol/water mixture and with methanol, and finally dried at 40 °C in vacuum oven. The product was characterized by elemental analysis (halide content) and by NMR.

Degrees of functionalization of these macroinitiators were estimated from the halide contents using a relation between the degree of functionality and content of the corresponding halide. For macroinitiators, functionalized with 2-bromoisobutyryl groups, formula (1) was used, where F is a degree of functionalization, 79.9 is atomic weight of bromine, 246 is molecular weight of the cellulose diacetate unit and 149.9 is molecular weight of 2-bromoisobutyryl group:

$$\mathrm{Br}(\%) = \frac{79.9F}{246 + 149.9F} \times 100 \quad (1)$$

Similar formula (2) was used in treatment of dichloroacetyl-containing macroinitiators; here, 70.9 is molecular weight of chlorine and 111.9 molecular weight of dichloroacetyl group:

$$\mathrm{Cl}(\%) = \frac{70.9F}{246 + 111.9F} \times 100 \quad (2)$$

The calculation of functionality from the halide content was verified by ^{1}H NMR analysis of dichloroacetyl-containing macroinitiators in dioxane, see below.

2.3. Graft copolymerization

CDA (0.4 g) functionalized with 0.10 dichloroacetyl group per CDA unit, 0.026 g (0.23 mmol) of CuCl and 0.015 g (0.12 mmol) of $CuCl_2$ was placed in a 25 ml round-bottom flask equipped with magnetic stirring bar and three-way stopcock, and repeatedly evacuated and flushed with argon. Then, 5 ml of 1,4-dioxane and 6.1 ml (57.5 mmol) of MMA were added, the macroinitiator was dissolved under stirring at room temperature and the flask content subjected to three freeze–thaw cycles. Finally, 0.062 ml (0.23 mmol) of HMTETA was added with a syringe, the mixture was heated to 90 °C in oil-bath and polymerized under stirring 2.5 h. After that, the reaction mixture was quickly cooled in ice-bath, diluted with 5 ml of THF and precipitated into 20-fold excess of an 8/2 (v/v) methanol/water mixture. The precipitation was repeated to remove residual catalyst and, finally, the product was dried at 40 °C in vacuum oven. In all experiments, monomer conversion was determined from the yield of

Table 1
CDA-macroinitiators

No.	Acyl halide	B[a]	Time (h)	Halide content[b] (%)	Degree of functionalization[c] (F)	SEC[d]	
						M_n	M_w/M_n
Br-CDA 1	BriB-Br	3.1:1	24	12.78	0.52	19,100	1.90
Br-CDA 2	BriB-Br	0.3:1	24	3.50	0.12	19,500	1.87
Cl-CDA 1	ClAc-Cl	1:1	20	2.90	0.10	22,100	1.84
Cl-CDA 2	ClAc-Cl	4:1	22	9.95	0.41	24,700	2.17

[a] Haloacyl halide/OH groups in CDA mole ratio.
[b] From elemental analysis.
[c] The number of haloacyl groups per CDA unit, see formulas (1) and (2) in Section 2.
[d] Eluograms were treated as CDA.

carefully isolated and purified product, from which the amount of used macroinitiator was subtracted. Also, length of grafts in product was calculated from the amount of monomer consumed during the grafting and from the content of active sites in the used macroinitiator, assuming that all of them were active in the initiation. The results of this method were verified by ^{1}H NMR analysis of poly(CDA-*g*-St), run 3, Table 2. The spectrum and the obtained data are given below.

2.4. Analysis of polymers

Molecular weights and polydispersities of macroinitiators and resulting graft copolymers were determined by SEC using a Labora HP-5001 set (Czech Republic) in THF at 20 °C with two 300 mm × 8 mm separation columns (PSS Germany) filled with SDV gel (particle size 5 μm, porosity 10^5 and 10^6 Å), equipped with differential refractometer Labora RIDK 102 and UV detector Labora LCD 2040. The flow rate of THF was 1 ml/min, the system with separation range 10^3–10^6 Da was calibrated with PMMA or polystyrene standards (PSS Germany). The eluograms of CDA macroinitiators were treated as CDA, those of copolymers with PMMA grafts as PMMA, eluograms of poly(CDA-*g*-St) as polystyrene [25] and eluograms of poly(CDA-*g*-BuA) as poly(2-ethylhexyl acrylate) [26]. It has to be noted that the calculated molecular weights of macroinitiators as well as those of copolymers are only apparent values.

NMR analysis: 300.13 MHz ^{1}H NMR spectra of the polymer solutions in tetrahydrofuran-d_8 were measured at 330 K with a Bruker Avance DPX300 spectrometer using HMDSO as an internal standard (position 0.05 ppm). Typically, 16 scans with 32 kilopoints were collected with 10 s repetition time in a quadrature detection and Fourier transformed into a 16 kilopoints spectrum without exponential weighting. The signals were assigned using a ^{1}H COSY spectrum.

3. Results and discussion

3.1. Synthesis of macroinitiators

Cellulose diacetate (CDA) was used as the starting material for preparation of ATRP macroinitiators. An average molecular weight of one CDA unit is 246. To obtain products with various contents of 2-bromoisobutyryl (BriB) or dichloroacetyl (ClAc) groups, 2-bromoisobutyryl bromide or dichloroacetyl chloride were used in various amounts relative to the amount of CDA, having in average one hydroxygroup per CDA unit. Thus, ca. 3-fold excess of BriB-Br was used in the first case and product with 12.78% of Br was obtained. Using formula (1), mentioned in Section 2, it can be estimated that this

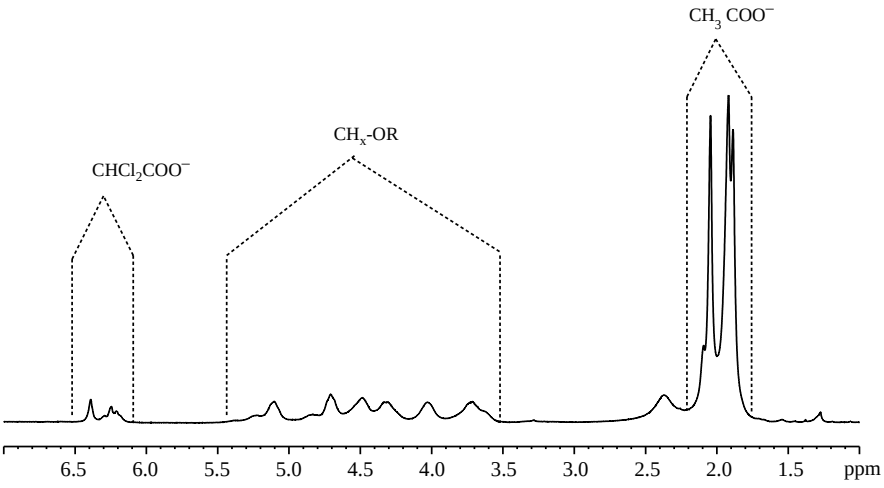


Fig. 1. 300.13 MHz ^{1}H NMR spectrum of Cl-CDA 2 macroinitiator (dioxan, 330 K), Table 1.

Table 2
Grafting of styrene from Br-functionalized CDA macroinitiators

Run	Initiator	F^a	Z^b	Time (h)	Conv. (%)	SEC[c]		DP[d]
						M_n	M_w/M_n	
1	Br-CDA 2	0.12	270	10	9	62,700	1.93	25
2	Br-CDA 2	0.12	680	12	14	104,500	1.95	100
3	Br-CDA 1	0.52	230	12	7	89,600	1.74	16
4	Br-CDA 1	0.52	440	9	13	113,800	1.89	58

[a] Functionality of macroinitiator.
[b] Styrene/BriB groups mole ratio.
[c] Calculated as PSt.
[d] Estimated average degree of polymerization of grafts.

macroinitiator (Br-CDA 1 in Table 1) contains approximately 0.52 2-bromoisobutyryl group per one CDA unit. In the second case, BriB-Br/CDA mole ratio was 0.30 only and acylation was performed under the same conditions. Here, the product contained 3.50% of bromine, so that the macroinitiator was obtained, having 0.12 2-bromoisobutyryl (BriB) group per CDA unit (Br-CDA 2, Table 1).

To prepare the chlorine-containing macroinitiator Cl-CDA 1 (Table 1), CDA was acylated with one equivalent of dichloroacetyl chloride relative to the concentration of hydroxy groups in CDA. The product contained 2.90% of chlorine, which corresponds to the degree of functionalization ca. 0.10, as calculated using formula (2). Further, CDA was acylated with 4-fold excess of dichloroacetyl chloride and the reaction product contained 9.95% of chlorine; thus, the Cl-CDA 2 macroinitiator contains ca. 0.41 dichlorocetyl group (ClAc) per CDA unit. Functionality of the dichloroacetyl-containing macroinitiators was checked by NMR, the ^{1}H NMR spectrum of Cl-CDA 2 macroinitiator is given in Fig. 1. Functionality 0.42 was calculated from the ratio of intensities of Cl_2CH–O groups at 6.2–6.5 ppm and CH_3CO groups at 1.7–2.2 ppm, which is in a good agreement with the functionality determined by elemental analysis. For Cl-CDA 1 macroinitiator, functionality 0.11 was obtained from NMR; again, perfectly corresponding to the result of elemental analysis. The prepared CDA macroinitiators and their characteristics are presented in Table 1. It is seen that CDA can be in this way functionalized in a wide range of densities of reactive groups, either BriB or ClAc in this case, which gives a possibility to prepare graft copolymers with various densities of grafts.

3.2. Grafting of BriB-functionalized CDA with styrene

Styrene grafting was initiated with Br-CDA macroinitiators (Table 1) having 2-bromoisobutyryl (BriB) initiating sites. The initiating system BriB/CuCl/$CuCl_2$/HMTETA with mole ratio 1/1/0.5/1 was used in all these polymerizations performed in dioxane at 110 °C. Due to a poor solubility of Br-CDA macroinitiators in styrene monomer, in particular that with the lower content of functional groups, dioxane had to be used in the amount at least equal to that of styrene. The results are summarized in Table 2. In runs 1 and 2, macroinitiator Br-CDA 2 was used, with 0.12 BriB group per one CDA unit, i.e. with rather low degree of functionalization. The amount of dioxane was 1.8 times higher than that of the monomer in both the runs; the excess of styrene over the concentration of BriB groups was ca. 270 in run 1 and 680 in run 2. Run 1 was polymerized at the given temperature for 10 h with styrene conversion ca. 9%. As calculated from the concentrations of functional groups and the amount of the consumed styrene, the approximate average length of the formed grafts was ca. 25 styrene units. Run 2 with 2.5 times higher excess of styrene over the initiator was polymerized for 12 h. Within this time interval, 14% of styrene was consumed, giving a copolymer with longer grafts, the DP of which was ca. 100. Thus, these two experiments led to

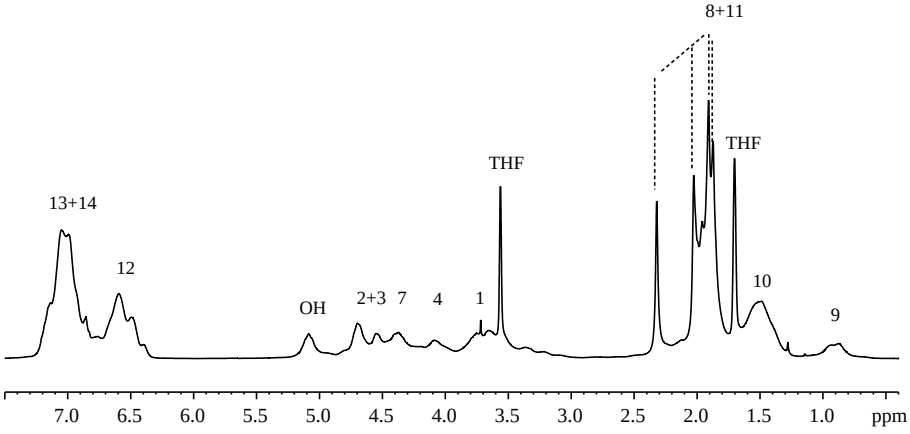


Fig. 2. 300.13 MHz ^{1}H NMR spectrum of poly(CDA-*g*-St), (tetrahydrofuran-d_8, 330 K), run 3, Table 2. The signal assignment corresponds to Scheme 1.

Table 3
Grafting of BuA from Br-functionalized CDA macroinitiators

Run	Initiator	F^a	Z^b	Time (h)	Conv. (%)	SEC[c]		DP[d]
						M_n	M_w/M_n	
1	Br-CDA 1	0.52	440	8.5	15	304,000	1.51	68
2	Br-CDA 2	0.12	410	5	25	173,600	1.68	106

[a] Functionality of macroinitiator.
[b] BuA/BriB groups mole ratio.
[c] Calculated as poly(2-ethylhexyl acrylate).
[d] Estimated degree of polymerization of the grafts.

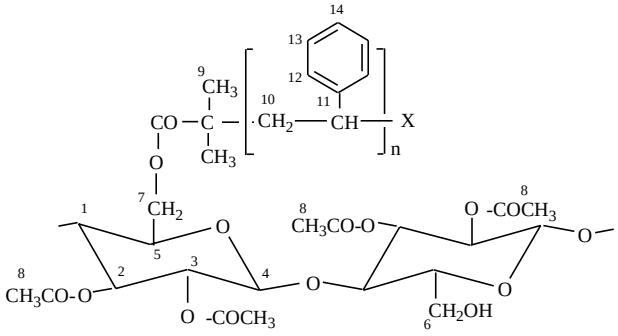
copolymers with rather low grafting densities (ca. 12 grafts per 100 CDA units) with different lengths of the grafts.

Runs 3 and 4 represent styrene graft copolymerizations initiated with densely functionalized macroinitiator Br-CDA 1, bearing 0.52 BriB group per one CDA unit. The same volume of dioxane as that of the monomer was added due to the better solubility of Br-CDA 1 in this solvent than that of Br-CDA 2 (see above). Excess of styrene was ca. 230 in run 3 and 440 in run 4. In run 3, 7% styrene conversion was achieved after 12 h polymerization, forming a graft copolymer with PSt grafts having DP ca. 16. Thus, the copolymer densely grafted with short grafts (ca. 52 grafts per 100 CDA units) was prepared in this experiment. In run 4, polymerization time was 12 h again and, due to the higher monomer concentration than in run 3, styrene conversion of 13% was achieved. Degree of polymerization of the formed PSt grafts can be estimated as 58, i.e. ca. 3.5 times longer than in run 3. The experiments in Table 2 clearly show that the method of functionalization and graft copolymerization allow to synthesize poly(CDA-*g*-styrene) copolymers with various and controllable density and length of PSt grafts.

Determination of length of PSt grafts from stoichiomeric conditions and monomer conversion was checked by NMR. ^{1}H NMR spectrum of poly(CDA-*g*-St) copolymer, run 3 in Table 2 is given in Fig. 2, where the signal assignment corresponds to Scheme 1 in which X represents terminal halogen atom. The St/CDA ratio was calculated from the integral intensities of signals (12+13+14) (*A*) and either (8+10+11) (*B*, after subtraction of the THF signal) or (1+2+3+4+5+6+7) (*C*), according to the formula (3). The difference between the two ways of calculation was below 7% rel. Thus, the St/CDA mole ratio is 6.7 as calculated in this way. Dividing this value by the degree of functionalization of macroinitiator, i.e. 0.52, average DP of the grafts equal to ca. 13 is obtained. This is in fair agreement with DP = 16, which was determined from the concentration conditions in the polymerization and monomer conversion.

$$\frac{\mathrm{St}}{\mathrm{CDA}} = \frac{6A}{5B-3A} = \frac{7A}{5C} \qquad (3)$$

A simple kinetic study of St graft copolymerization was performed in order to get information about 'livingness' of the process. In run 2, Table 2, aliquots of the reaction mixture were withdrawn after selected time intervals, products were isolated, dried, weighed and analyzed by SEC. Monomer conversion was thus determined from the polymer yield in each sample. The dependence of $\ln[M]_0/[M]$ on reaction time in Fig. 3 is linear in the time interval from 0 to ca. 14 h documenting thus virtually constant concentration of active chains and, therefore, a controlled process, at least within this time period and conversion range. Molecular weight of the formed copolymer, calculated as PSt from SEC eluograms increases with growing monomer conversion. However, MWDs of individual samples are unimodal up to conversion ca. 15%; after this value, MWD of the copolymer becomes clearly bimodal. This is shown in Fig. 4, where trace 1 belongs to the product obtained after 6 h,



Scheme 1. Poly(CDA-*g*-St) copolymer.

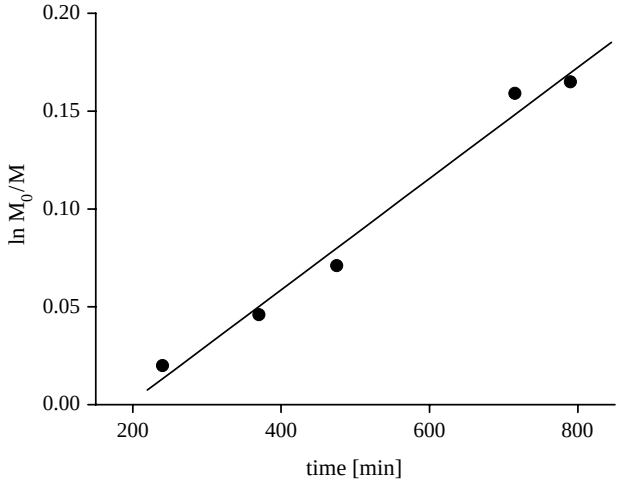


Fig. 3. Semilogarithmic dependence of monomer consumption on time for styrene polymerization initiated with BriB-functionalized CDA; run 2, Table 2.

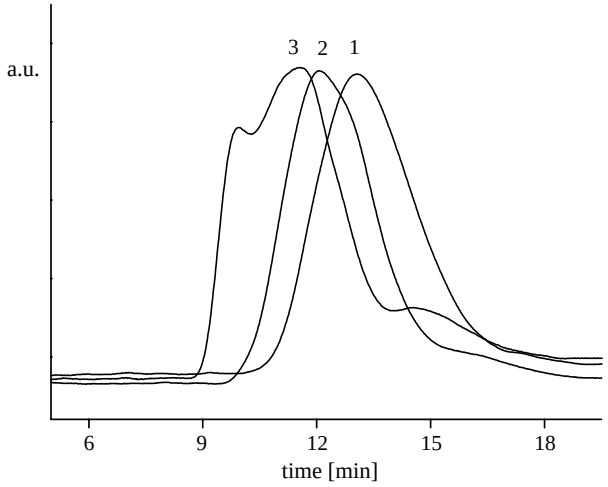


Fig. 4. Development of molecular weight distributions of the product in dependence on polymerization time and monomer conversion; for conditions see run 2, Table 2. Trace 1, 6 h, 4.5%; trace 2, 12 h, 14%; trace 3, 20 h, 29%.

(St conversion 4.5%), trace 2 to that formed after 12 h (conversion 14%) and trace 3 represents the copolymer, obtained after 20 h polymerization (29% monomer conversion). The last eluogram, trace 3, is clearly bimodal with a new peak at a shorter elution time. It can be reasonably assumed that this part of the product, having a distinctly higher molecular weight, was formed by intermolecular recombination of growing grafts. This is why rather low monomer conversion is recommended in the graft copolymerization.

Two poly(CDA-*g*-St) copolymers, the both with grafting densities 0.12 and different lengths of the grafts, were extracted with cyclohexane (good solvent for St homopolymer) to check an extent of possible St homopolymerization, accompanying the copolymerization. It was found, that only very small amounts of the samples dissolved (1–2% w/w). Thus, it can be assumed that the extent of homopolymerization, leading to polystyrene, is virtually negligible.

3.3. Grafting of BriB-functionalized CDA with BuA

Further, Br-CDA 1 and Br-CDA 2 macroinitiators with BriB functional groups were used for grafting of BuA. Both the copolymerizations were performed in acetone and in the presence of PMDETA as the complexing ligand; Cu powder was added to speed-up the reaction. In run 1, Table 3, Br-CDA 1 macroinitiator was used, densely functionalized with BriB groups and BuA/BriB mole ratio was 440. The BriB/CuCl/Cu/PMDETA mole ratio was 1/1/3/2 and acetone/BuA volume ratio 1/1.75 in this case. After 8.5 h polymerization at 60 °C, 15% of the monomer was consumed and the obtained soft and sticky copolymer had a unimodal MWD. Calculated from the concentration conditions and BuA conversion, DP of the grafts was ca. 68. In run 2, polymerization was initiated with Br-CDA 2 macroinitiator, less densely grafted with 0.12 BriB group per CDA unit. The mole ratio of reaction components BriB/CuCl/Cu/PMDETA was 1/1/1/2, BuA was added in 410-fold excess over the concentration of BriB groups. The acetone content in this reaction mixture was the same as in the foregoing experiment and reaction temperature was 70 °C. Polymerization was faster than in run 1 so that the monomer conversion of 25% was achieved after 5 h polymerization. Again, the product with unimodal MWD was soft and sticky and contained PBuA grafts with DP ca. 106 in this case, as calculated from concentration conditions.

Table 4
Grafting of MMA from Cl-functionalized CDA macroinitiators

Run	Initiator	F^a	Z^b	Time (h)	Conv. (%)	SEC[c]		DP[d]
						M_n	M_w/M_n	
1	Cl-CDA 1	0.10	380	1.5	18	122,600	2.04	69
2	Cl-CDA 1	0.10	710	2.5	21	232,000	1.95	163
3	Cl-CDA 2	0.41	1240	6.5	3	193,300	1.69	34
4	Cl-CDA 2	0.41	1240	18	7	282,400	1.52	88

[a] Functionality of macroinitiator.
[b] MMA/functional ClAc groups mole ratio.
[c] Calculated as PMMA.
[d] Estimated total length of the PMMA grafts (see below).

Table 5
Graft copolymers with block-copolymer-type grafts

Run	Macroinitiator	F^a	Z^b	Time (h)	Conv. (%)	SEC[c]		DP[d]
						M_n	M_w/M_n	
1	Run 1, Table 2	0.12	720	20	5	182,300	2.38	34
2	Run 1, Table 4	0.10	580	27	10	302,000	2.58	55

[a] Grafting density in a number of grafts per CDA unit.
[b] BuA/functional halide groups.
[c] Calculated as PMMA.
[d] Estimated degree of polymerization of PBuA blocks.

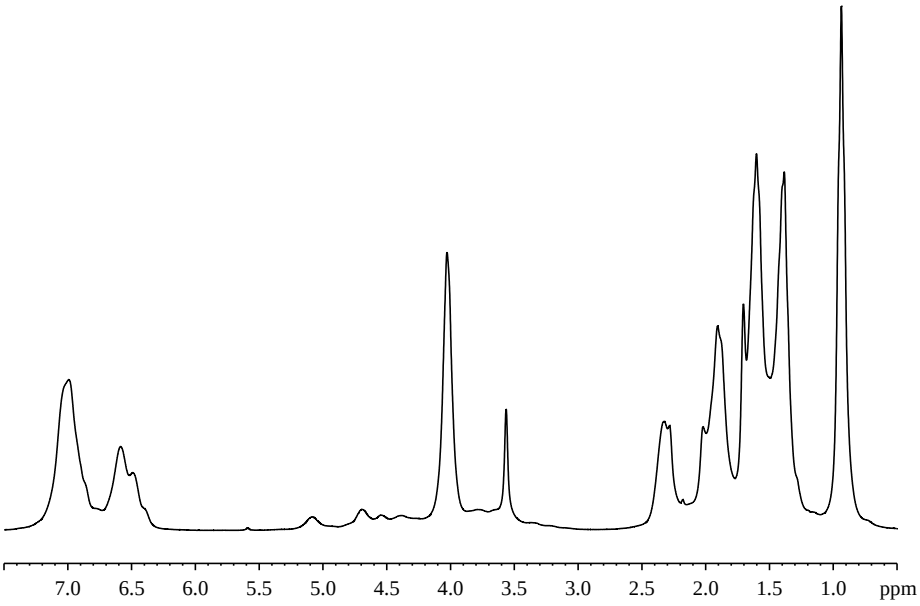


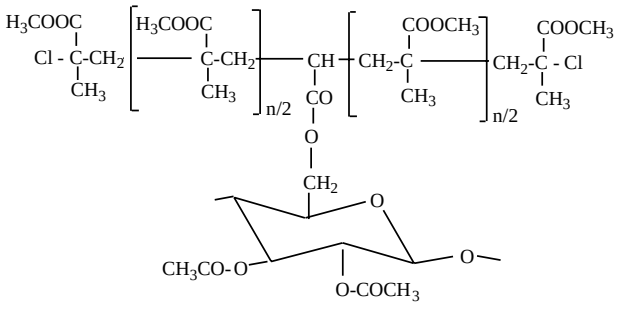
Fig. 5. ^{1}H NMR spectrum of: 3-poly[CDA-*g*-(St-*b*-BuA)] copolymer, run 1, Table 4.

3.4. Grafting of ClAc-functionalized CDA with MMA

Here, two initiating systems with different composition were used. In the first experiment, run 1 in Table 4, polymerization was initiated with Cl-CDA 1 macroinitiator having ca. 1 ClAc group per 10 CDA units and the ClAc/CuCl/$CuCl_2$/HMTETA mole ratio was 1/1/0.5/1. The reaction was performed at 90 °C in dioxane. The dioxane/MMA volume ratio was 1/1.2 and MMA was added in 380-fold excess with respect to the estimated concentration of ClAc initiating groups. Polymerization time was rather short to keep the monomer conversion low, which is recommended with respect to a possible recombination of growing grafts at high conversions, when the concentration of residual monomer is low. Thus, the reaction was stopped after 1.5 h at MMA conversion 18%. The obtained product with rather low grafting density had unimolecular, slightly broadened MWD with PDI = 2.04. The average degree of polymerization of PMMA grafts was calculated as 69. The second experiment (run 2, Table 4) was an attempt to prepare a copolymer with the same grafting density but with longer PMMA grafts; the mole ratio of MMA to dichloroacetyl groups was 710 in this case. The dioxane/MMA volume ratio was the same as in the foregoing experiment, i.e. 1/1.2. The polymerization was initiated with the same macroinitiator Cl-CDA 1; however, the ClAc/CuCl/$CuCl_2$/HMTETA mole ratio was 1/2/1/2. The polymerization was terminated after 2.5 h and MMA conversion 21%. The isolated product was poly(CDA-*g*-MMA) with the estimated DP of the grafts ca. 163. Thus, runs 1 and 2 are graft copolymers with rather low grafting density, i.e. ca. 1 graft per 10 CDA units, assuming that all ClAc functional groups of the macroinitiator were efficient in MMA polymerization.

In the next experiments, runs 3 and 4, polymerization was initiated with densely functionalized Cl-CDA 2 macroinitiator, having ca. 0.41 functional group per CDA unit, (Table 1). The polymerizations were performed at 75 °C, with bPy as the ligand with the ClAc/CuCl/$CuCl_2$/bPy mole ratio 1/2/1/4 and in the presence of dioxane in concentration 2.5 times lower than that of MMA. Monomer concentration was 1240 times higher than the content of the macroinitiator functional groups. Polymerization was slow, so that in run 3 monomer conversion was ca. 3% only after 6.5 h. Nevertheless, due to the high excess of MMA over initiating sites, graft copolymer was formed in a good yield, having PMMA grafts with DP ca. 34. The same reaction conditions were used in run 4, only polymerization time was prolonged up to 18 h; monomer conversion 7% was achieved and the grafts of the formed copolymer had DP 88. Thus, runs 3 and 4 are poly(CDA-*g*-MMA) copolymers with high grafting density and different lengths of grafts.

It has to be noted, that dichloroacetate in conjunction with CuCl/bPy catalysis was in literature reported as bifunctional initiator of acrylate ATRP [27]. In contrast, dichloroacetyl groups, anchored on various calixarenes and combined with $[RuCl_2(PPh_3)_3]$ catalyst and $Al(OiPr)_3$ activator, act as monofunctional initiators in which only one chlorine atom



Scheme 2. Poly(CDA-*g*-MMA) copolymer.

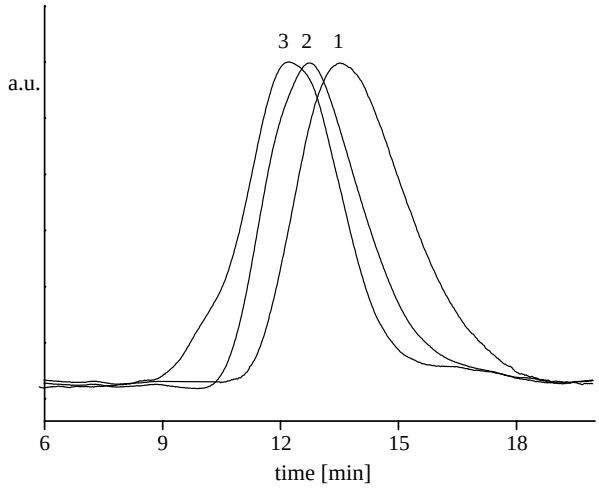


Fig. 6. SEC traces of: 3-poly[CDA-*g*-(St-*b*-BuA)], run 1, Table 5; 2-poly(CDA-*g*-St), run 1, Table 2 and 1-Br-CDA 1 macroinitiator, Table 1.

initiates ATRP of MMA whereas the other does not react [28]. Therefore, it can be assumed that dichloroacetyl groups bound on CDA chain and used in this work can also be bifunctional initiating sites, giving probably PMMA grafts composed of two 'branches'. The functionality of the dichloroacetyl groups was verified by NMR analysis of two low-molecular-weight PMMAs (M_n = 1800 and 2900, respectively, by SEC), prepared by ATRP initiated with methyl dichloroacetate. M_n values, calculated from the integrated intensities of OCH_3 protons in the terminal methacrylate units at 3.82 ppm and those of the MMA units in the chain at 3.58 ppm, were 2080 and 2900. This documents bifunctionality of dichloroacetyl groups anchored on CDA. Therefore, the PMMA grafts are likely composed of two branches according to Scheme 2, with average lengths equal to one half of the corresponding DP values, given in Table 4.

3.5. Synthesis of graft copolymers with diblock grafts

The graft copolymers poly(CDA-*g*-St) and poly(CDA-*g*-MMA) were further used as macroinitiators of BuA polymerization in order to obtain products with block-copolymer-type grafts (Table 5). In run 1, BuA polymerization was initiated with poly(CDA-*g*-St) (run 1, Table 2), under CuCl/PMDETA catalysis. The mole ratio of halogenated styrene units (Scheme 1) to CuCl and to PMDETA was 1/1/2; the excess of BuA over initiating sites was ca. 720. Acetone was used as a solvent in the amount equal to one half of that of BuA. After 20 h polymerization at 60 °C, BuA conversion reached 5% and DP of BuA blocks in the grafts was ca. 34, as calculated from stoichiometric conditions and BuA conversion. This estimation was verified by ^{1}H NMR analysis of the copolymer; the spectrum is given in Fig. 5. As calculated from the integrated intensities of peaks of styrene aromatic protons at 6.5–7.3 ppm and methylene protons of BuA OCH_2 groups at 4.1 ppm, St/BuA mole ratio of styrene and BuA units was 0.73. This is in an excellent agreement with the same mole ratio, calculated from the lengths of PSt and PBuA blocks in grafts as 0.74. Also, polydispersities of the final product and the macroinitiator are not too different; M_w/M_n = 2.38 and 2.13, respectively. SEC traces of poly[CDA-*g*-(St-*b*-BuA)], poly(CDA-*g*-St) and the corresponding Br-CDA macroinitiator indicate 100% initiating efficiency in both the polymerization steps (Fig. 6).

The next experiment, run 2, was initiated with poly(CDA-*g*-MMA) copolymer (run 1, Table 4), the BuA/MMA-Cl (Scheme 2) mole ratio was 580 under otherwise the same conditions as in run 1. After 27 h polymerization, ca. 10% of BuA was consumed and the resulting product was thus graft

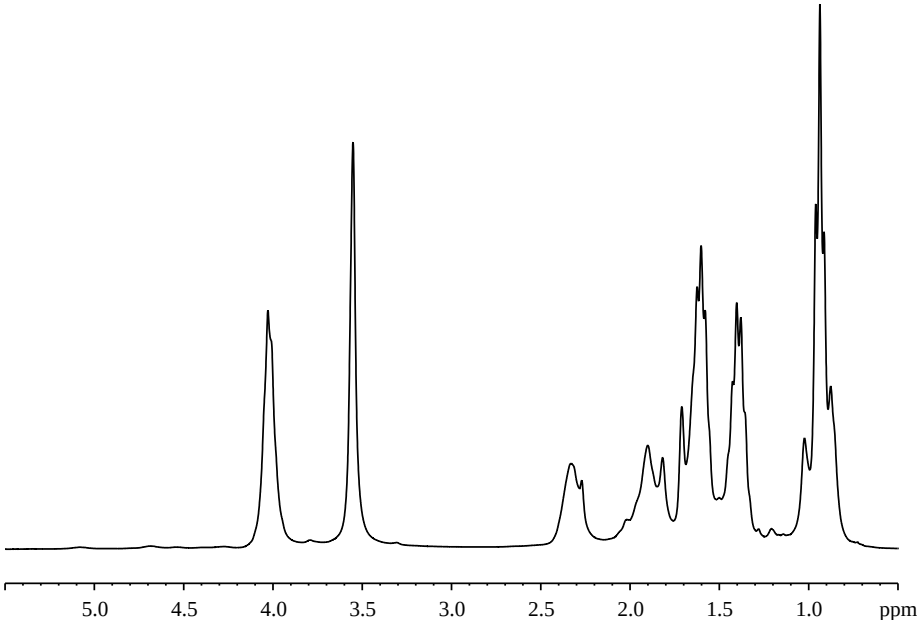


Fig. 7. ^{1}H NMR spectrum of: 3-poly[CDA-*g*-(MMA-*b*-BuA)] copolymer, run 2, Table 4.

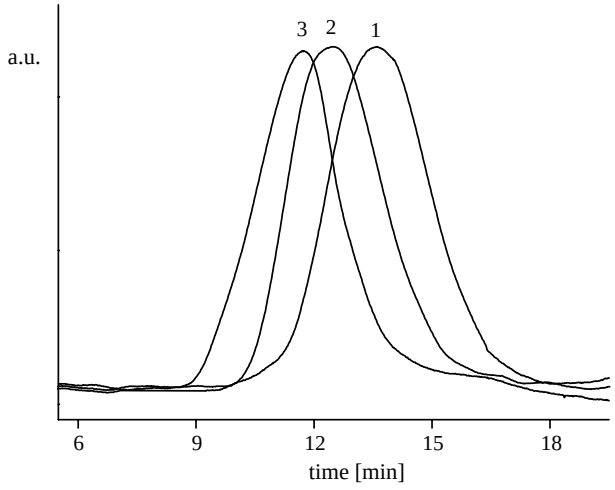


Fig. 8. SEC traces of: 3-poly[CDA-*g*-(MMA-*b*-BuA)], run 2, Table 5; 2-poly(CDA-*g*-MMA), run 1, Table 4 and 1-Cl-CDA 1 macroinitiator, Table 1.

copolymer with poly(MMA-*b*-BuA) grafts containing PBuA blocks with DP = 55 as calculated from concentration conditions and BuA conversion. Again, the product was analyzed by ^{1}H NMR (Fig. 7). The MMA/BuA mole ratio in the grafts was calculated from signals of protons of MMA OCH_3 groups at 3.5 ppm and protons of BuA OCH_2 groups at 4.0 ppm; the result, 0.69, fairly corresponds to the MMA/BuA ratio 0.63, calculated from the lengths of blocks. SEC eluograms in Fig. 8 again indicate virtually quantitative initiating efficiencies of the Cl-CDA 1 macroinitiator and poly(CDA-*g*-MMA) copolymer in the corresponding polymerization steps. Let us note that poly(MMA-*b*-BuA) grafts also consist of two branches due to the fact that the poly(CDA-*g*-MMA) precursor was prepared using CDA, functionalized with bifunctional dichloroacetyl groups (see above). Therefore, these grafts are in fact ABA-type triblock copolymers, where A is PBuA and B PMMA, linked to the CDA backbone likely in the middle of the central PMMA block. Thus, the total number of BuA units in both the PBuA outer blocks is twice higher than the DP value in Table 5, i.e. ca. 110.

4. Conclusion

ATRP active sites were introduced into cellulose diacetate by acylation of residual hydroxy groups with 2-bromoisobutyryl bromide or dichloroacetyl chloride, and the degree of functionalization was varied in a wide range (0.10–0.52 functional group per CDA unit). The polyfunctional macroinitiators, prepared in this way were subsequently used for grafting polymerization of St, MMA and BuA. Under properly chosen reaction conditions, lengths of the grafts can vary in a wide range; however, monomer conversions have to be low to avoid formation of branched or even insoluble products. Moreover, block-copolymer type grafts can be easily prepared using graft copolymers with terminal halide groups as macroinitiators. Thus, the described method affords a wide scale of graft copolymers with CDA backbone and grafts of various density, length and chemical structure, having expectedly various application and mechanical properties.

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