Synthesis of Block and Grafted Copolymers Containing Spacer-Linked Chromophore Based on Cellulose and Polyethylene Glycol

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Received 18 November 2003; accepted 29 March 2004
DOI 10.1002/app.21026
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of block copolymers from hydroxyl-terminated cellulose triacetate (HCTA) and cellulose triacetate (CTA) with polyethylene glycol (PEG) were prepared. To activate terminal acid groups in the polyethylene glycols, acid groups were first converted to the acetyl groups with chlorination reaction. In the second series, the cellulose triacetate, having fully substituted acetate groups, was hydrolyzed by the acid catalyst method by using acetic acid and small percentages of water. Then cellulose derivatives containing 4-(4-nitrophenylazo)-1-naphthol (Magneson II) as a chromophore and long hydrocarbon side chains were prepared. The compound 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene was first synthesized from 4-(4-nitrophenylazo)-1-naphthol and 1,4-dibromobutane. The alkylated chromophore reacted with prepared cellulosic and oligocellulosic copolymers in the solution of dimethyl sulfoxide to produce cellulose ethers having the desired chromophore. Polymers containing a mixture of alkyl side chains were also prepared by the addition of 1-bromododecane to the reaction mixture. The above method was used for the preparation of (dodecyl) [4′-butoxy-4-(4-nitrophenylazo)naphthalene] (CTA-*co*-PEG2000) and (dodecyl) [4′-butoxy-4-(4-nitrophenylazo)naphthalene] (HCTA-*co*-PEG2000). The structure of products was determined by FTIR, ^{1}H-NMR spectroscopy, GPC, and the intrinsic viscosity measurement. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1175–1185, 2004

Key words: cellulose triacetate; oligomers; block copolymers; graft copolymers; magneson II chromophore

INTRODUCTION

Block and graft copolymers, composed of polysaccharide, have become of considerable interest because of their many unique properties. Block copolymers of oligomeric species containing terminated hydroxyl groups of cellulose triacetate (CTA) with various diisocyanated molecules have been reported.[1–5] This type of copolymers have shown novel elastomeric,[6] biodegradable,[7] and water sorption[8] properties in various applications and as biomedically active materials.[9] A variety of cellulose ethers have been reported that show to be suitable materials for the fabrication of ultrathin films by the Langmuir–Blodgett (LB) technique, and the incompletely etherified cellulose ethers, which contain free hydroxyl functions, are interesting materials for LB multilayer assembly with respect to their potential applications.[10]

Isogai et al.[11] compared three different nonaqueous cellulose solvents for preparing tri-*O*-benzylcellulose. The three solvents were the N_2O_4–dimethyl sulfoxide (DMSO), SO_2–diethylamine (DEA)–DMSO, and LiCl–dimethylacetamide (DMAC) systems. The authors concluded that of the three nonaqueous cellulose solvents, the SO_2–DEA–DMSO system was the best for the preparation of benzylcellulose. Isogai and coworkers successfully used the same solvent to prepare a large variety of tri-*O*-alkyl cellulose products. The alternative approach for the preparation of cellulose ethers under homogeneous reaction conditions was reported by Kondo et al.[12] These authors used soluble cellulose derivatives as starting materials rather than cellulose alkyl ethers, which were prepared from cellulose itself. In this way, fully substituted cellulose alkyl ethers were prepared from cellulose triacetate in DMSO solution.[13]

In this article we report the adaptation of this method to the preparation of cellulosic and oligocellulosic copolymers having polysaccharides and polyethylene glycol blocks in the chain backbone, which contain 4-(4-nitrophenylazo)-1-naphthol as the chromophore. The obtained compounds have potential applications in noncentrosymmetric structures for second-order nonlinear optics (NLO).[14–19]

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EXPERIMENTAL

Materials and measurements

Cellulose triacetate (CTA) was purchased from Fluka (Buchs, Switzerland; M_w, 72,000–74,000) and was dried at 105°C for 3 h in air before use. 1-Bromododecane was prepared from 1-dodecanol (Merck, Darmstadt, Germany) according to a literature method. Polyethylene glycol 600 diacid, polyethylene glycol 2000, and 4-(4-nitrophenylazo)-1-naphthol (Merck) were used without further purification.

^{1}H-NMR spectra were recorded on a Bruker NMR 400-MHz spectrometer (Karlsruhe, Germany); IR spectra were recorded on a Shimadzu model FT-IR 8101N spectrometer (Kyoto, Japan); GPC analyses were performed using a GPC Waters (Milford, MA) 150°C with PS as the standard (column, ultra styragel 10^4, 10^5, and 10^6Å; detector, RI; flow rate 1.0 mL/min; column temperature 30°C); viscosimetry was performed using an Oswald viscometer; Perkin-Elmer differential scanning calorimeter (DSC; Perkin Elmer Cetus Instruments, Norwalk, CT) was used to determine the thermal transitions of the polymers and the scanning rate was 10°C/min.

Depolymerization of CTA

CTA was depolymerized in 99.4% acetic acid solution using a modified procedure[2]: 20 g cellulose triacetate (inherent viscosity 6.37 dL/g in DMF, t = 25°C) was depolymerized using 200 g hot glacial acetic acid solution (99.9%). A quantity of 3.3 mL of acetic anhydride was added to the solution of cellulose triacetate, then 1.0 mL concentrated sulfuric acid was added as catalyst in 2 min. To the solution 1.2 mL water was added and the mixture was stirred at 80°C for 7 h and cooled to 35°C. The catalyst was neutralized by adding 15 mL of a 21% aqueous solution of $Mg(AcO)_2$ to the reaction. The resulting product was produced with the addition of excess diethyl ether in which a milky precipitate was formed. The precipitant was washed with ethanol (10 mL) then washed with water (10 mL). The obtained product was soluble in dichloromethane.

Acylation of acid-terminated polyethylene glycol 600

The dried acid-terminated polyethylene glycol 600 (3.12 mmol carboxylic acid groups, 1.0 g) was placed in a 10-mL round-bottom flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer. The reaction flask was equipped with a calcium chloride tube, an empty trap, and a trap with a NaOH solution (2N) on the top of the condenser, to exclude moisture and absorption of HCl and SO_2. Then $SOCl_2$ (3 mL, 35 mmol) was added dropwise at 0°C over a period of 30 min into the flask. The temperature was slowly increased to room temperature over 1 h and finally was maintained at 70°C for 6 h; the excess of $SOCl_2$ was distilled off under vacuum at 40°C. Then 10 mL CH_2Cl_2 or toluene was added to the solution and solvents were evaporated azeotropically under vacuum to remove the traces of $SOCl_2$. The acylated polyethylene glycol 600 was washed with petroleum ether, and the obtained product was a viscous oil.

Chlorinating of polyethylene glycol 2000

These precursors were chlorinated according to the above-mentioned method; however, the final stage of precipitation was performed in diethyl ether instead of petroleum ether and both ranges of polyethylene glycol and their chlorinated derivatives were soluble in CH_2Cl_2 and CH_3Cl. Some of the physical properties of the compounds were measured.

Preparation of copolymers

Graft copolymerization of CTA with Cl–PEG–Cl, 600

The fully substituted cellulose triacetate (92% acetylated) containing 8% of free OH groups, which randomly distributed in different positions of cellubiose unit along the CTA chain as starting material, was chosen. To substitute the OH groups with chlorine group, to form Cl–PEG–Cl, 600, CTA (6.1 g, 2.6 mmol hydroxyl groups, 0.0834 mmol CTA) was dissolved in 50 mL CH_2Cl_2 in a 100-mL three-neck round-bottom flask equipped with a dropping funnel, magnetic stirrer, Ar inlet, and efficient reflux condenser connected to a $CaCl_2$ drying tube. Then a solution of Cl–PEG–Cl, 600 (1.7 g, 5.2 mmol acyl chloride groups) in 5 mL CH_2Cl_2 was added to the CTA solution at room temperature under vigorous stirring. After 2 h a solution of pyridine (0.21 g, 2.6 mmol) in 5 mL CH_2Cl_2 was added dropwise and the reaction mixture was warmed gently with continued stirring in a water bath with gentle refluxing for 50 h. The solvent of reaction mixture was evaporated. The obtained oily compound was treated with 25 mL of MeOH/H_2O (7/3, v/v) after filtering, yielding a yellow-white compound. For further purification the compound was dissolved in CH_2CL_2 and was then poured into MeOH/H_2O (7/3, v/v) and dried under vacuum. The different experiments were applied to the evaluation of the physical properties.

Block copolymerization of HCTA with Cl–PEG–Cl, 600

In a 100-mL two-neck round-bottom flask with an agitator and a Dean–Stark trap, with condenser and drying tube, HCTA (2 mmol) was dissolved in a mix-

ture of ethylene chloride (50 mL) and ethylene chloride (25 mL). The mixture was azeotropically distilled to collect 25 mL of distillate. For the copolymerization a solution of HCTA (1.78 g, 5.2 mmol hydroxyl groups, 1.3 mmol HCTA), compound Cl–PEG–Cl, 600 (2.33 g, 6.4 mmol acetyl groups), and pyridine (0.55 g, 7 mmol) were mixed and refluxed for 45 h. The resulting product was filtered through a sintered-glass filter and most of the solvent was removed by evaporating. The obtained oil was treated with 25 mL MeOH/H_2O (9/1, v/v). The physical properties such as viscosity, melting point, and solubility were evaluated.

Graft copolymerization of CTA with Cl–PEG–Cl, 2000

To the solution of CTA (2.7 g, 1.15 mmol hydroxyl groups, 0.037 mmol CTA), compound Cl–PEG–Cl, 2000 (3.36 g, 3.2 mmol acetyl groups) and pyridine (0.31 g, 4 mmol) were added according to the method mentioned in the preceding experiment.

Block copolymerization of HCTA with Cl–PEG–Cl, 2000

A solution of HCTA (0.81 g, 2.30 mmol hydroxyl groups, 0.59 mmol HCTA), compound Cl–PEG–Cl, 2000 (3.36 g, 3.2 mmol acetyl groups), and pyridine (0.31 g, 4 mmol) as the catalyst was mixed according to the method mentioned above and the different experiments were applied to the evaluation of the physicochemical properties of the resulting compound.

Preparation of 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene

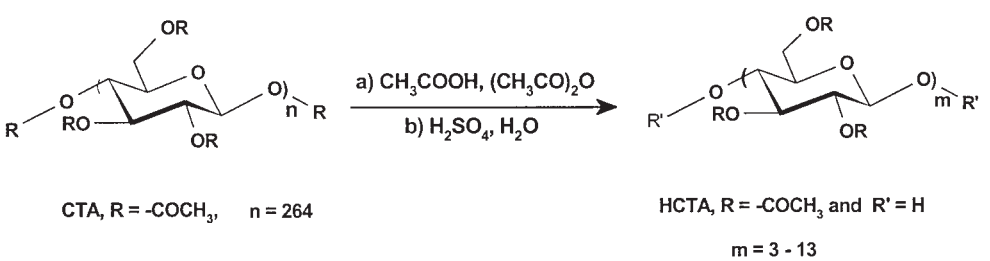
A solution containing 4-(4-nitrophenylazo)-1-naphthol (1 g, 3.4 mmol), dichloromethane (100 mL), benzyltriethylammonium chloride (800 mg), and aqueous sodium hydroxide 50% (50 mL) was prepared. Then about 10-fold excess molar relative to chromophore from 1,4-dibromobutane was added and the mixture was stirred at 40°C for 1 h. The dichloromethane was removed by evaporation and the residue extracted with chloroform. The chloroform layer was washed with water and dried over Na_2SO_4 overnight. The chloroform was evaporated and excess dibromobutane was removed by heating to 80°C under vacuum. Recrystallization of the final product with different solvents failed. Therefore, purification was accomplished with column chromatography using *n*-hexane/dichloromethane (2/1, v/v) as eluent. The first compound was the desired compound as a solid, mp 136°C.

Preparation of cellulose ethers containing chromophore

The cellulosic and oligocellulosic copolymers containing the desired chromophore were prepared by adapting a literature method[12] for the synthesis of cellulose ethers. Copolymer (0.25 g) was dissolved in a mixture of DMSO (30 mL) and water (0.5 mL) under nitrogen. After stirring at room temperature for 1 h, NaOH powder was added (12.5*M* excess relative to the three substitution sites per glucose unit). The solution was stirred for an additional hour, then was heated to t_1°C (see Table III) before the introduction of 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene. The reaction was allowed to proceed for time T_1, then was heated to t_2°C before the second alkylating agent, 1-bromododecane, was added. The reaction was allowed to continue for an additional time T_2. The two products (dodecyl) [4′-butoxy-4-(4-nitrophenylazo)naphthalene] (CTA-*co*-PEG2000) and (dodecyl) [4′-butoxy-4-(4-nitrophenylazo)naphthalene] (HCTA-*co*-PEG2000) were prepared by varying the reaction times, temperature, and amounts of alkylating reagents. The exact conditions are summarized in Table III. The resulting products were isolated by precipitation in 200 mL of MeOH/H_2O (7/3, v/v), followed by extraction with methylene chloride. The crude product was purified by repeated dissolution and precipitation in the solvent/nonsolvent pair of CH_2Cl_2 and mixture of MeOH/H_2O (7/3, v/v).

RESULTS AND DISCUSSION

Among the blocking groups, the acetyl blocking groups in the backbone of CTA were not inadvertently removed during the depolymerization reaction of pri-



Scheme 1 Depolymerization reaction of CTA in acidic conditions.

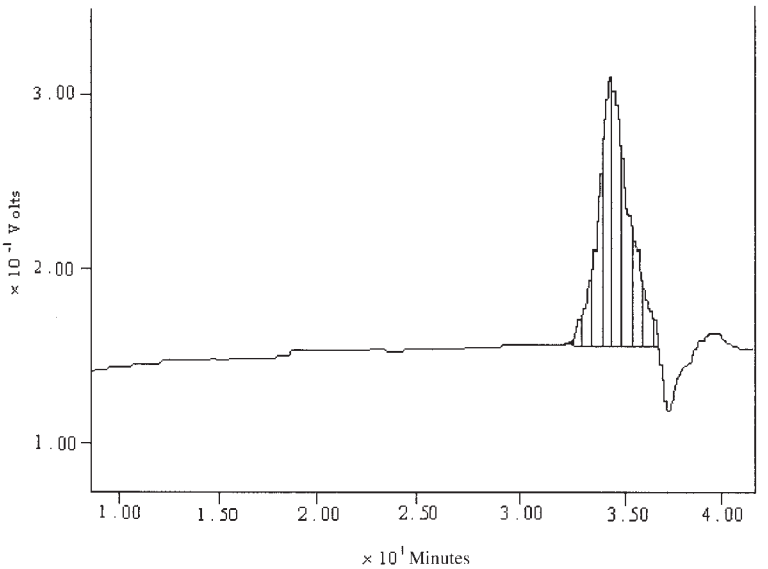


Figure 1 GPC chromatogram of HCTA.

mary CTA and the resistance of acetyl groups in the hydrolyzing reaction condition is relatively good and prevents additional blocking reactions. The degree of substitution (DS) of oligomeric blocks should be as close to 3 as possible. The molecular weights of CTA before hydrolyzing and after hydrolyzing (HCTA) were measured using a GPC instrument. The CTA gave a number-average molecular weight (M_n) of 73,000, whereas in the same condition the oligomeric cellulose (HCTA), M_n is 3748 with a polydispersity index of 1.4 (CTA, $n \approx 264$ gives HCTA, $n \approx 13$ and n is the number of anhydroglucose units) (Scheme 1).

The GPC chromatogram of HCTA is shown in Figure 1, which indicates relatively narrow molecular weight distributions. The DSC spectrum in Figure 2 indicates that the glass-transition temperature (T_g) of the HCTA oligomer is 220.71°C.

The FTIR spectrum shows that the expected relatively strong hydroxyl stretching absorption at 3508 cm^{-1} is attributed to the end groups and a strong carbonyl absorption at 1757 cm^{-1} to the acetyl groups of the obtained HTCA. Whenever as-purchased CTA (Fluka) contains the maximum 92% of acetyl groups, about 8% of hydroxyl sites situated on the anhydroglucose unit in the backbone still remain randomly as free hydroxyl groups. As shown in Scheme 2, CTA has free hydroxyl groups and HCTA reacted with PEG, which was previously converted to the acetylated forms.

The comparison of the ^{1}H-NMR spectra of CTA and produced copolymers (CTA-*co*-PEG600 and CTA-*co*-PEG2000) also confirmed the occurrence of the polycondensation reactions. As shown in Figure 3 the band in the ranges of 1.93–2.15 and 3.6–5.1 ppm is attrib-

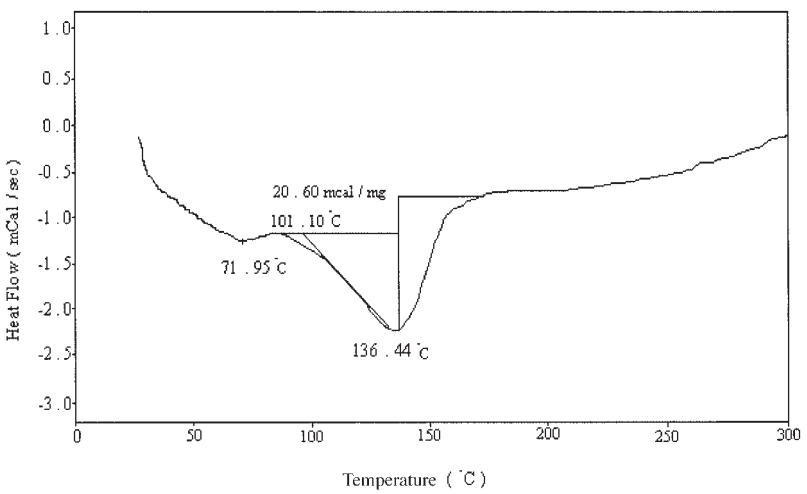
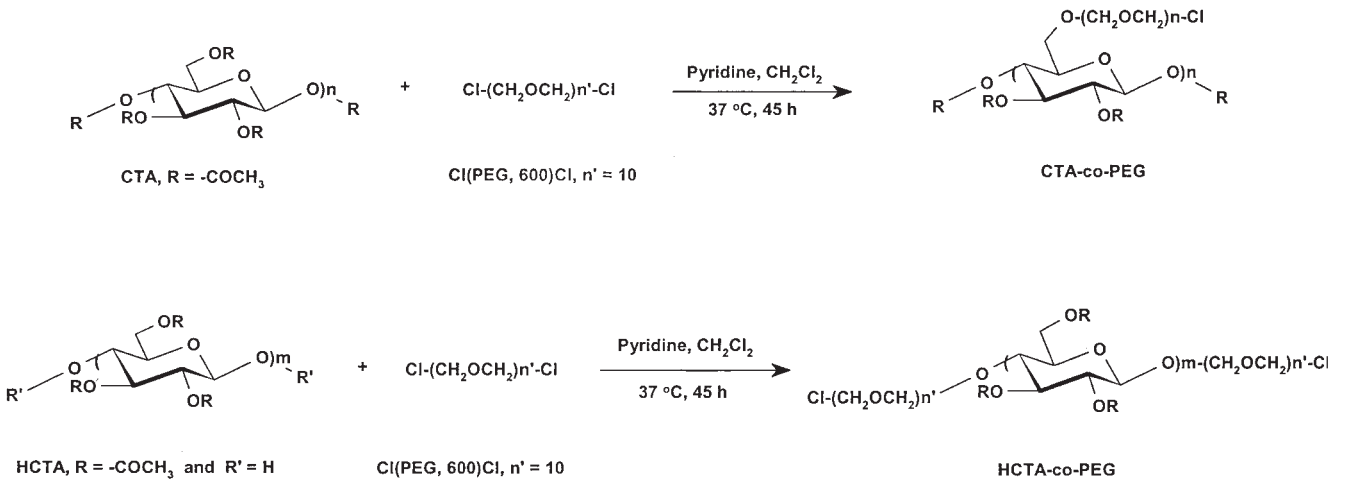


Figure 2 DSC chromatogram of HCTA.



Scheme 2 Preparation of CTA-*co*-PEG600 as a grafted copolymer and HCTA-*co*-PEG600 as a block copolymer.

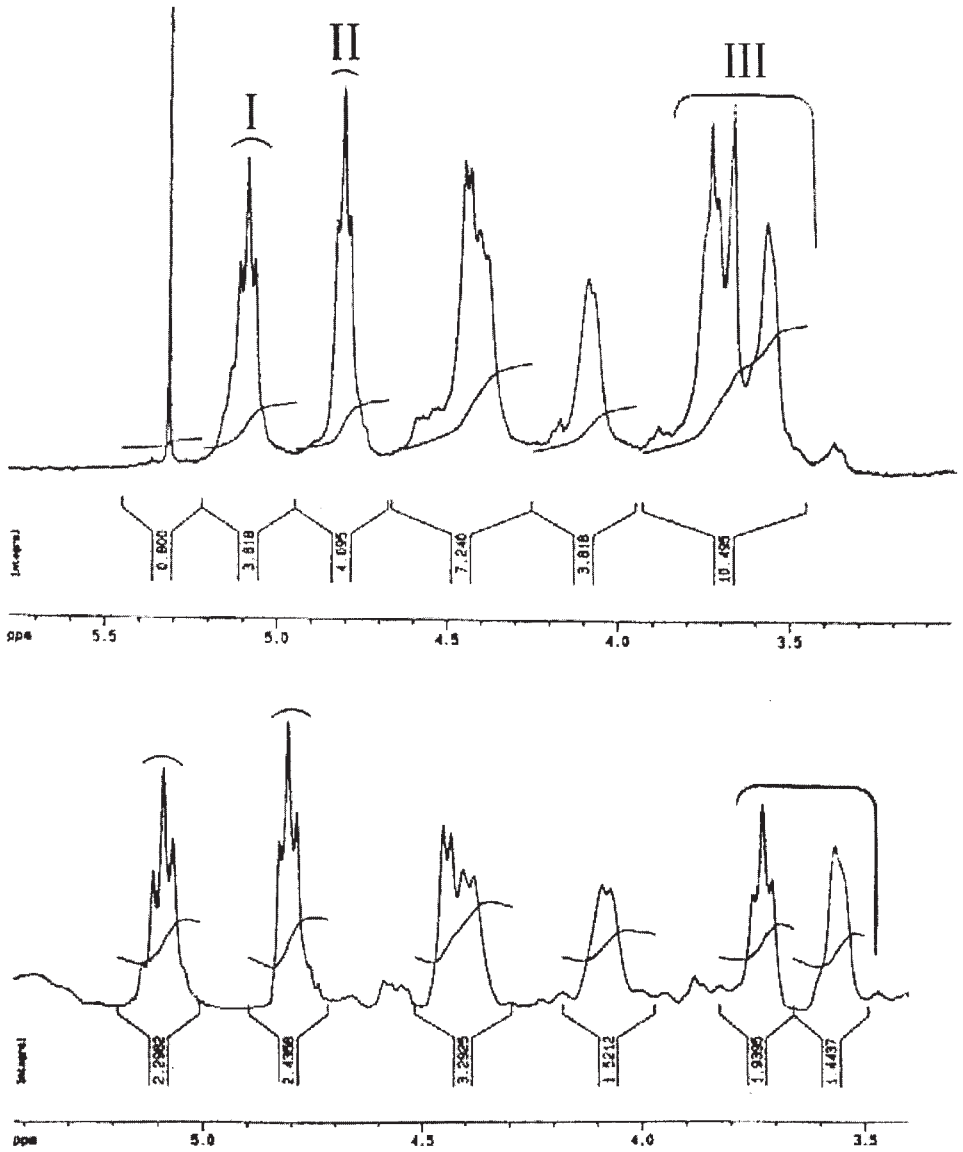
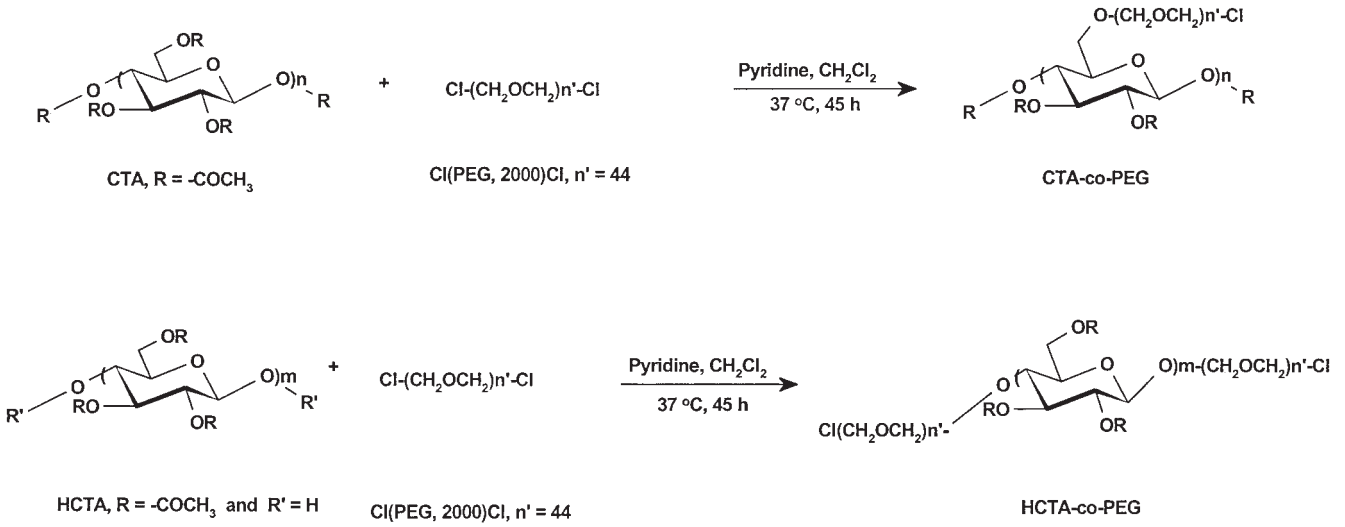


Figure 3 Comparison between ^{1}H-NMR spectra of CTA (top) and CTA-*co*-PEG600 (bottom) in $CDCl_3$ solution.



Scheme 3 Preparation of CTA-*co*-PEG2000 as a grafted copolymer and HCTA-*co*-PEG2000 as a block copolymer.

uted to the H of acetyl groups and glucose residues, respectively, both of CTA and CTA-*co*-PEG600 or CTA-*co*-PEG2000.

It was indicated that the ratios of selected protons integration II/I in both ^{1}H-NMR spectra of both above copolymers and CTA are approximately equivalent. However, the ratios of III/I are not equivalent. Thus:

$$\text{CTA:}\quad \text{II/I} = 2.435/2.298 = 1.059$$

$$\text{III} = 1.443 + 1.939 = 3.383 \quad \text{and}$$

$$\text{III/I} = 3.383/2.298 = 1.472$$

$$\text{Copolymer:}\quad \text{II/I} = 4.095/3.818 = 1.072 \quad \text{and}$$

$$\text{III/I} = 10.495/3.818 = 2.748$$

The enhancement of ratio III/I in copolymeric sample indicates the connection of PEG to the CTA and the bands at 3.55–3.75 ppm imply the etheric CH_2 groups from PEG600 and PEG2000. In other words, the integration of 10.495 instead of 5.620 is evidence of the formation of the product, given that

$$\text{CTA:}\quad \text{III/I} = 1.472$$

$$\text{Copolymer:}\quad \text{I} = 3.818$$

then, the calculated integration:

$$\text{III} = 1.472 \times 3.818 = 5.620$$

The comparison of ^{1}H-NMR spectra of HCTA-*co*-PEG600 (or HCTA-*co*-PEG2000) and HCTA similar to

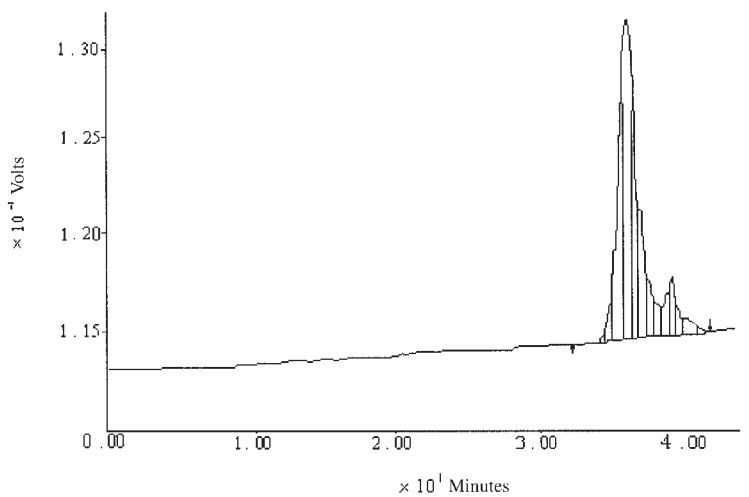


Figure 4 GPC chromatogram of HCTA-*co*-PEG2000.

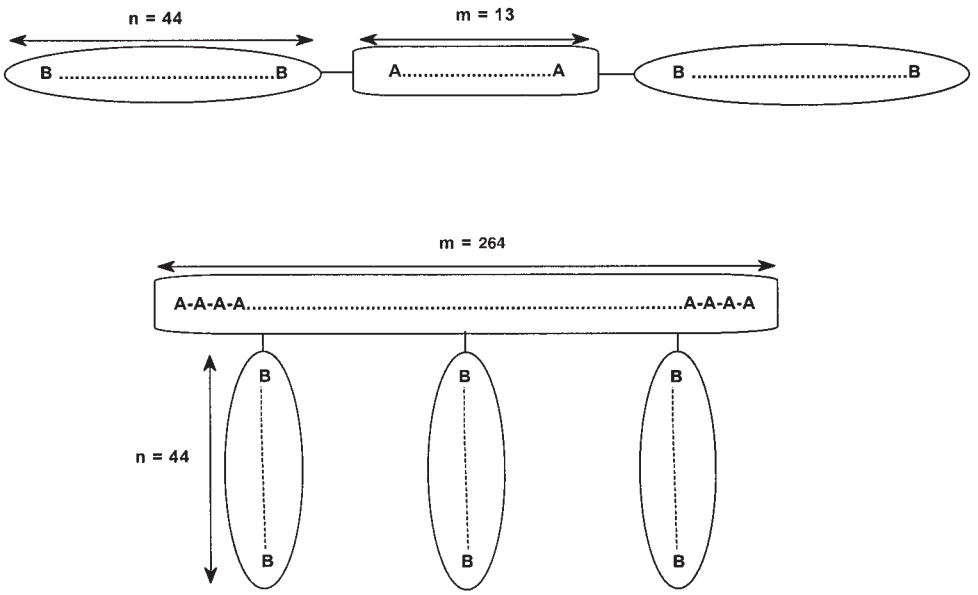


Figure 5 Suggested structure of HCTA-*co*-PEG2000: **A** = HCTA and **B** = PEG2000; and CTA-*co*-PEG2000, **A** = CTA and **B** = PEG2000.

the above shows that the enhancement intensity at 3.55–3.75 ppm belongs to the etheric CH_2 groups for PEG in copolymers, which is also evidence of the formation of copolymeric products.

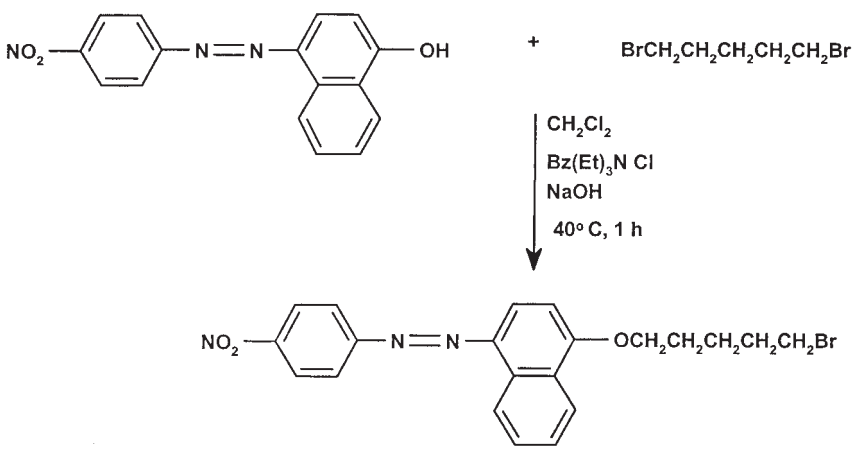
In the reaction of PEG2000 with CTA and HCTA (Scheme 3), in comparison to the reaction of PEG600, the presence of a higher number of repeated monomers in the backbone of HCTA-*co*-PEG2000 copolymer causes the solubility of the products to be similar to the solubility property of PEG in common polar solvents, and its solubility in the purification step is increased. To maximize the yield of the products and to separate the unreacted PEG from the products, the solvent systems of MeOH/H_2O (7/3, v/v) and MeOH/H_2O (9/1, v/v) were applied for the CTA and HCTA, respectively.

To access the copolymer with structure PEG–HCTA–PEG, excess molar (PEG2000)Cl was reacted with HCTA. In Figure 4 the GPC chromatogram of HCTA-*co*-PEG2000, which indicates the average number of molecular weight 7592 with polydispersity of 1.4, is shown. By calculations from the molecular weight it was determined that the PEG was connected to the end sides of the hydroxyl groups in the HCTA molecule.

The schematic structure of the block copolymer is shown in Figure 5. The DSC spectrum of HCTA-*co*-PEG2000 block copolymer shows a T_g of 71.95°C.

The GPC chromatogram of isolated copolymer CTA-*co*-PEG2000 indicated the number-average molecular weight of 164,991 and polydispersity of 2.1.

In Figure 5 the schematic structure of grafted PEG2000 to the CTA backbone is shown.



Scheme 4 Preparation of 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene.

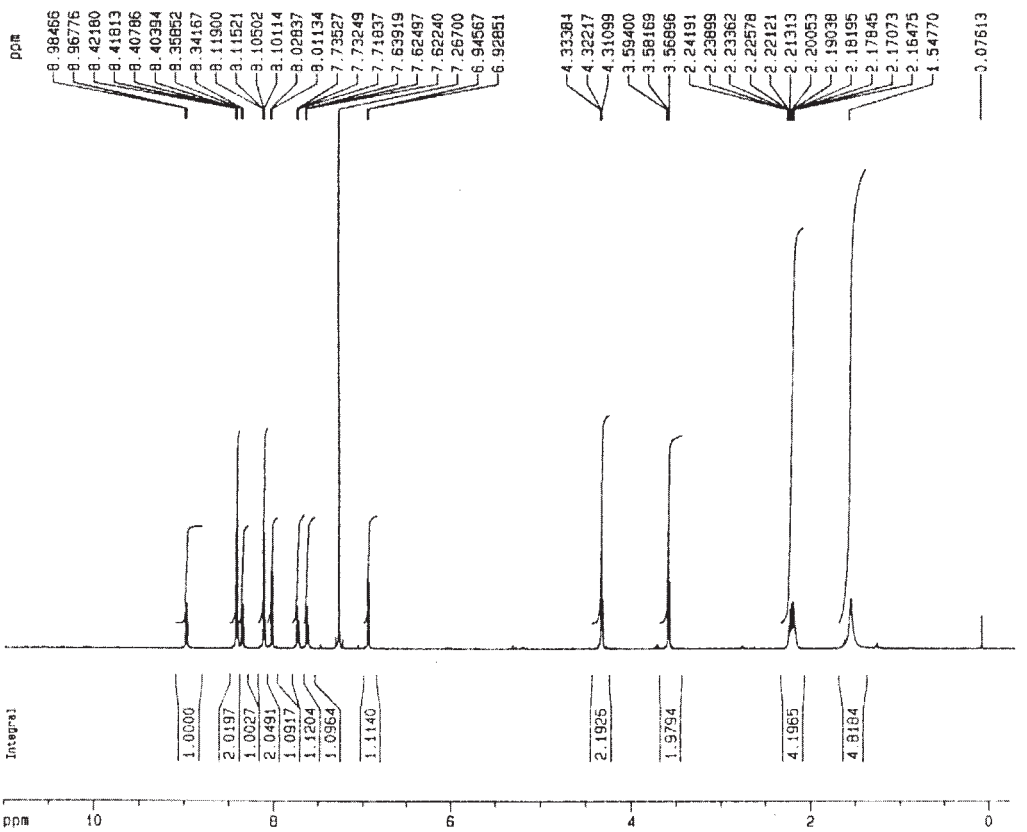
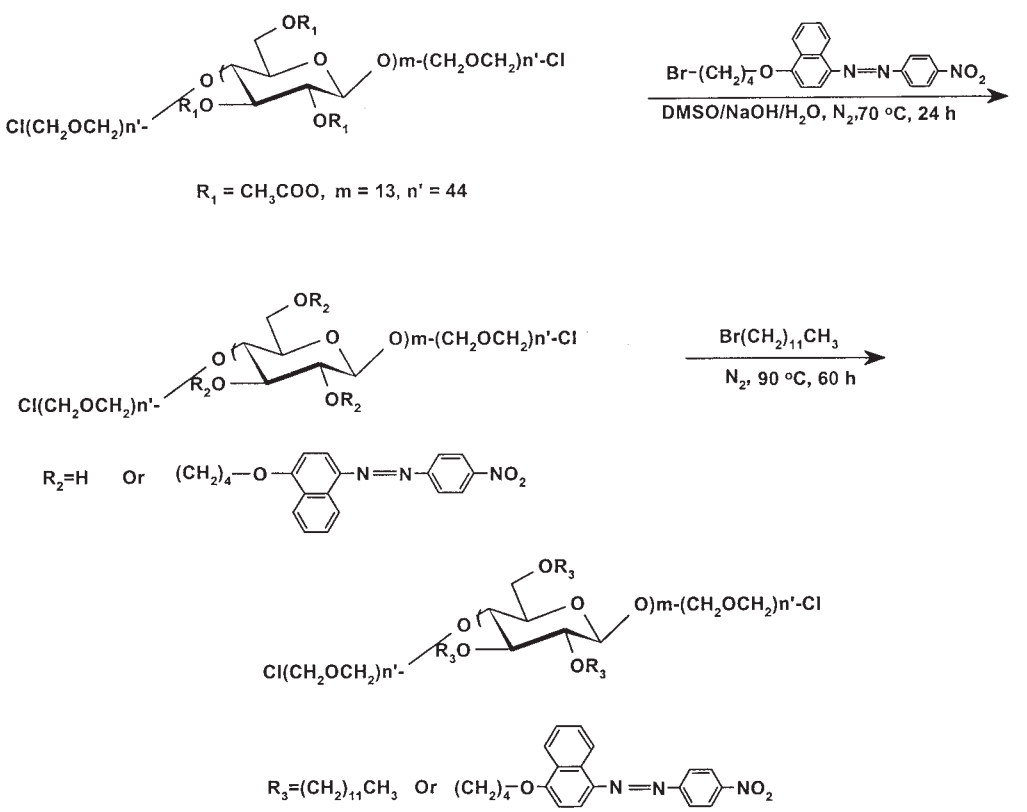


Figure 6 ^{1}H-NMR spectra of 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene in $CDCl_3$ solution.



Scheme 5 General reaction used for the preparation of decorated hairy rod amphiphiles of cellulose, oligocellulose, and its copolymers.

TABLE I
Physical Data of the Various Ranges of Acylated or Chlorinated Polyethylene Glycols and HCTA

	CTA	HCTA	Cl-PEG-Cl, 600	Cl-PEG-Cl, 2000
State of matter	Granol	Powder	Oil	Powder
Color	Withe	Withe	Light yellow	yellow-orange
mp in °C	119	187–188	—	59
Solution in CH_2Cl_2	+	+	+	+
$[\eta]$ in dL/g[a]	6.37	1.92	0.37	0.97
Yield in %	—	89	100	95

[a] DMF as solvent at 25°C.

With simple calculation, as in the following, it was concluded that about 66 free hydroxyl sites exist along the backbone of CTA in the starting material:

Molecular weight of four anhydroglucose units without any substitution:

$$\mathbf{m} = C_6H_7O_5 = 159$$

Molecular weight of anhydroglucose unit with three substituted acetyl groups:

$$\mathbf{a} = 3(CH_3CO) + 159 \rightarrow \mathbf{a} = 3(43) + 159 = 288$$

Molecular weight of anhydroglucose unit with two acetyl groups and one free hydroxyl group:

$$\mathbf{b} = 2(CH_3CO) + 1(H) + 159 \rightarrow \mathbf{b} = 2(43) + 1 = 246$$

Molecular weight of four anhydroglucose units containing substituted acetyl groups and free hydroxyl groups in 92% cellulose backbone:

$$\mathbf{c} = 3\mathbf{a} + \mathbf{b} \rightarrow \mathbf{c} = 3(288) + 1(246) = 1110$$

Average molecular weight of anhydroglucose unit in 92% cellulose backbone:

$$\mathbf{n} = 1110/4 \approx 277$$

$$\mathbf{DP_n} = 73{,}000/277 \approx 264$$

(CTA, $M_n \approx 73000$;

$DP_n \approx 264$ with total acetylation 92%)

The number of the hydroxyl groups in 92% cellulose triacetate (CTA) backbone:

$$266/4 = 66$$

Therefore, from 264 glucose units in the CTA backbone there are 66 free hydroxyl groups. The diffrence between two molecular weights of copolymer and starting material:

$$164{,}991\ (\text{GPC}) - 73{,}000\ (\text{GPC}) = 91991$$

This number indicates the molecular weight of PEG grafted to the CTA backbone. Thus, the number of free hydroxyl groups, or the number of total grafted PEGs, is

$$91991/2000 \approx 46$$

To produce the cellulosic copolymers containing chromophore, 4-(4-nitrophenylazo)-1-naphthol (magneson II) was chosen from the available compounds. The target compounds have potential applications for the fabrication of ultrathin films by the LB technique, in the study of NLO properties. The chromophore magneson II has some advantage for this purpose because of its proper structure. To activate the magneson II it was reacted with excess 1,4-dibromobutane, and 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene was obtained (Scheme 4).

The ^{1}H-NMR spectrum in Figure 6 shows the aromatic protons at the regions between 6.62 and 8.98 ppm, with relative integration 10.7, and aliphatic protons between 2.16 and 4.33 ppm, with relative integration 8.4 corresponding to 10H and 8H aromatic aliphatic protons, respectively.

The reaction consists of a base-catalyzed deacetylation to generate the cellulose alkoxide ion, which in turn reacts with the alkyl halide to produce desired compounds. Here, the cellulose copolymers containing 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene were prepared by a two-step alkylation procedure, outlined in Scheme 5.

Tables I and II detail the physical data of starting materials and copolymers, respectively.

As shown in Table III various reaction conditions were used to obtain a series of products (denoted with letters **a** and **b**). In general, partial alkylation of cellulose by 4′-bromobutoxy-4-(4-nitrophenylazo)naphthalene was achieved in the first step of the reaction

TABLE II
Physical Data Relative to the Copolymers of CTA and HCTA with PEG 600 and PEG 2000

Copolymer	mp (°C)	$[\eta]$[b]	Yield (%)
CTA-*co*-PEG, 600	163	6.43	67
HCTA-*co*-PEG, 600	124	2.04	62
CTA-*co*-PEG, 2000	167	6.58	70
HCTA-*co*-PEG, 2000	137	2.41	56

[a] Prepared copolymers are completely soluble in CH_2Cl_2 and $CHCl_3$.
[b] DMF as solvent at 25°C.

TABLE III
Reaction Conditions Used for the Preparation of Copolymers of (Dodecyl) [4′-butoxy-4-(4-nitrophenylazo)naphthalene]: CTA-*co*-PEG2000 and HCTA-*co*-PEG2000[a]

Sample	Step 1 (R-Br)[b]	T_1 (h)	t_1 (°C)	Step 2 (R-Br)	T_2 (h)	t_2 (°C)
a[c]	3.95 (3.3)	23	70	11.5 (20)	60	90
b[c]	3.95 (3.3)	23	70	13.5 (20)	40	80

[a] T_1 and T_2 are reaction times; t_1 and t_2 are temperatures.
[b] The quantity of alkylating agent (R-Br) added in each step is given as molar equivalents relative to the three substitution sites on the anhydroglucose ring in bracets. The alkylating agents in step 1 is 4-bromobutoxy-4-(4-nitrophenylazo)naphthalene and 1-bromododecane in step 2.
[c] After 30 h from second step of alkylation 7 mL DMSO again was added to the reaction. **a,** CTA-*co*-PEG2000 and **b,** HCTA-*co*-PEG2000.

sequence followed by the subsequent substitution of unreacted sites with 1-bromododecane. The yields of products were around 90%. The compounds (dodecyl) [4′−butoxy-4-(4-nitrophenylazo)naphthalene] (CTA-*co*-PEG2000) and (dodecyl) [4′−butoxy-4-(4-nitrophenylazo)naphthalene] (HCTA-*co*-PEG2000) were successfully synthesized through the same procedure.

The FTIR spectra of the produced copolymers are shown in Figure 7. The absence of significant absorption at 1749 cm^{-1}, which is characteristic of carbonyl group frequency of CTA and HCTA blocks, demonstrates that deacetylation was completed. Moreover, the absence or the presence of very weak intensities of hydroxyl bands at 3300–3500 cm^{-1} for CTA-*co*-PEG2000 and HCTA-*co*-PEG2000, respectively, indicated that relatively high degrees of alkyl substitution were achieved. Moreover, the presence of a strong double branch band at 2860 and 2930 cm^{-1}, attributeded to CH_2 and CH_3 stretching vibrations, were representative of complete esterification of copolymers. It should be noted that the spectra presented in Figure 7 were recorded for sample films cast onto KBr substrates and, probably, a contribution from water cannot be neglected in the film spectra. The presence of the chromophore in samples **a** and **b** is clear from the characteristic vibrations at 2310, 1580,1525, 1464, 1385, 1300, and 777 cm^{-1}.

CONCLUSIONS

Chain-extension reactions were used to prepare block and graft copolymers. The obtained products were confirmed with ^{1}H-NMR and FTIR spectral and calculated intrinsic viscosity data. The spectrum of each copolymer contained absorption peaks corresponding to the blocked and grafted components. The copolymers were soluble in various organic solvents such as CH_2Cl_2, DMF, and DMSO. It could be concluded that the obtained copolymers have little crosslinking in their structures. Novel synthesized cellulosic and oli-

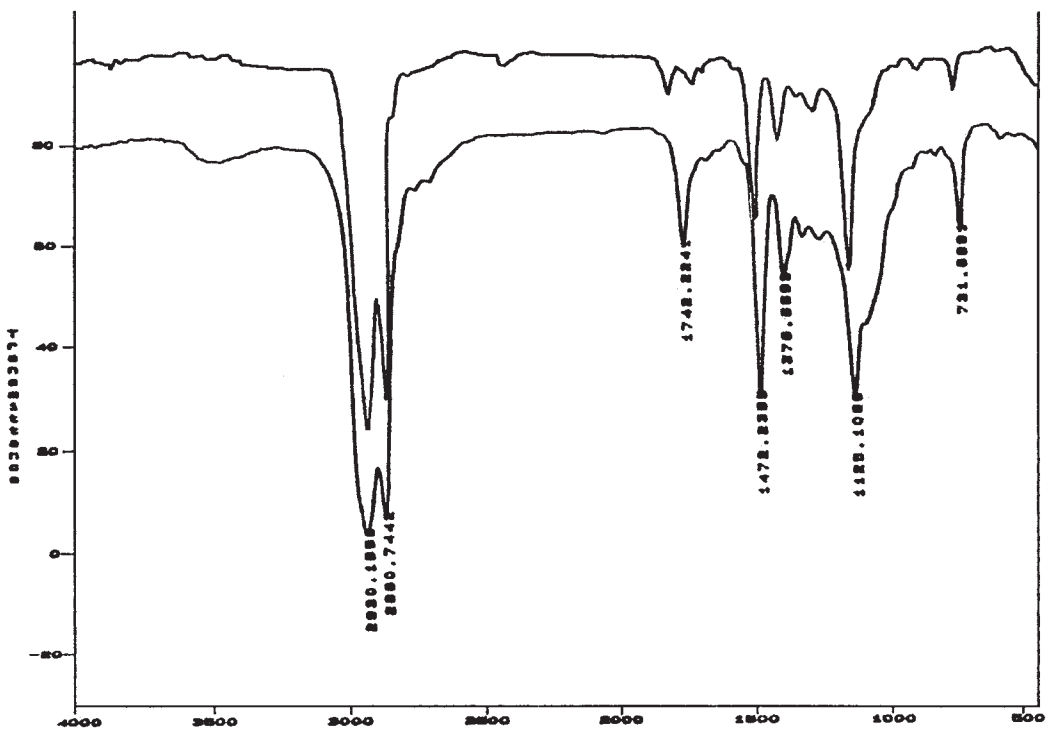


Figure 7 FTIR spectra of sample **a** (top) and **b** (bottom) as defined in Table III. Spectra were recorded from film cast onto KBr windows.

gocellulosic copolymers containing the 4-(4-nitrophenylazo)-1-naphthol chromophore can be conveniently prepared from cellulose triacetate and oligocellulose triacetate with 4′-bromobutoxy-4-(4-nitrophenylazo)-naphthalene and dodecylbromide. Highly substituted mixed ethers were obtained by the successive introduction of these two different alkylating agents.

This method also could be applied to the alkylation of other macromolecules that are soluble in DMSO, such as polyvinyl acetate, polyvinyl alcohol, chitin triacetate, and amylose triacetate and its copolymers.

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