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Synthesis of allyl cellulose in NaOH/urea aqueous solutions and its thiol-ene click reactions†

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Allyl celluloses (ACs) were synthesized by reacting cellulose with allyl chloride in NaOH/urea aqueous solutions. The reaction started homogeneously and ended heterogeneously. The structure and properties of ACs were characterized with SEC-LLS, NMR and solubility testing. The results demonstrated that organo-soluble AC, with a degree of substitution of 0.98-1.65, could be obtained by adjusting the molar ratio of allyl chloride to the anhydroglucose unit of cellulose. A capability evaluation of the click-reaction of AC was performed by selecting four thiol compounds. AC-click products were characterized with FT-IR, NMR and elemental analysis, and the results indicated few impurities or substructures resulting from side reactions. The click-reaction displayed a high conversion rate, and all the AC-click products demonstrated high solubility in certain solvents. This work provides a facile method for the synthesis of AC in an aqueous system, and shows a novel stage for the mild and diverse derivatization of cellulose.

1. Introduction

Cellulose is well-known for its utility in sustainable chemistry. It can be converted into various derivatives and regenerated materials.[1] Chemical modification of cellulose continues to be the most important route to structure and hence property design.[2] Recently, Sharpless et al introduced click chemistry, a modular approach that uses only the most practical and reliable transformations.[3] Compounds not accessible via etherification, esterification and other commonly applied reactions can be yielded through click reaction, which can significantly broaden the structural diversity of modified cellulose. Compared with one-step esterification or etherification, the "click" reaction is more suitable for cellulose derivatization as it requires only stoichiometric amounts of starting materials, and generates few by-products. In order to adapt "click" reaction for cellulose derivatization, carbon-carbon double/triple bond, thiol or azide modified cellulose should be prepared as the intermediate product. In the previous work, azide[4-7] and alkyne modified cellulose[8-10] have been successfully prepared as intermediate product in surface modification and derivatization of cellulose. The azide-alkyne reaction is fulfilling many processes, including atom economy, high yields, simple reaction conditions, fast reaction and high selectivity.[11,12] Compared with azide-alkyne click reaction, the thiol-ene reaction is milder and more environment-friendly, providing an efficient approach for both synthesis as well as surface modification.[13] However, carbon-carbon double bond[14-18] or thiol[19,20] modified cellulose that are reported in recent years usually have a low degree of substitution (DS), which significantly influences the click reaction and limits subsequent applications.

Allyl cellulose (AC) is a good intermediate product when producing various cellulose derivatives through click reaction. Sawatari et al reported the preparation of AC with DS of only 0.37 from alkali cellulose and allyl chloride in isopropanol.[21] In order to obtain AC with high DS, some studies have focused on using cellulose derivatives, such as cellulose acetate as starting material,[22] or utilizing a new cellulose solvent, such as DMSO/LiCl[23] or DMF/LiCl.[24] Recently, Heinze et al synthesized AC with the DS ranging from 0.5 to 2.98 in DMSO/TBAF.[25] NaOH/urea aqueous solution has been proved to be an ideal solvent for the etherification of cellulose, and various cellulose ethers have been successfully synthesized.[26-33] In this work, NaOH/urea was further used for the synthesis of AC. This was advantageous compared with previous researches using other solution systems due to its ability to proceed without organic solution or catalyst. The reaction started homogeneously but ended heterogeneously, which provides the product AC with a high DS and facilitates its purification. This organo-soluble AC could be used to produce a variety of cellulose derivatives through "click" reactions with different thiol compounds.

2. Experimental section

2.1. Materials

Microcrystalline cellulose (MCC) was supplied by Asahi Kasei Chemicals Corporation (Japan), and the degree of polymerization (DP) was 100-300. Allyl chloride, *n*-dodecyl mercaptan (NDM), 2-aminoethanethiol hydrochloride (AET), cysteine (Cys), monothioglycerol (MG) and other reagents were of analytical grade and used without further purification.

2.2. Synthesis of AC in NaOH/urea aqueous solutions

MCC was dissolved in NaOH/urea aqueous solutions according to previous method.[26] A certain amount of allyl chloride was added dropwise into 100 g MCC solution (4 wt%), and the mixture was stirred at 35 °C for 72 h under exclusion of light. The reaction

product was neutralized with HCl aq. and precipitated with acetone. The precipitate was washed with acetone and distilled water, and then freeze-dried with lyophilizer (Christ Alpha 1-2, Osterode am Harz, Germany) to obtain the purified AC. The obtained AC was stored at -20 °C under the exclusion of light. By changing the molar ratio of allyl chloride to the anhydroglucose unit (AGU) of cellulose from 9:1 to 24:1, four samples were obtained (Table 1).

2.3. Click reactions of AC with thiolcompounds

AC-NDM and AC-MG were synthesized according to the following procedure. First, a certain amount of AC was dissolved in 20 mL DMSO at 25 °C. Then, the respective thiol compounds and 2,2-dimethoxy-2-phenylacetophenone (7% molar ratio with respect to thiol groups) were added at an ambient temperature and the mixture was stirred under a nitrogen atmosphere under UV-radiation (365 nm) for 2 h. The product was dialyzed with regenerated cellulose tubes (M_w cutoff 8000, USA) against distilled water for 7 days, and finally freeze-dried with lyophilizer (Christ Alpha 1-2, Osterode am Harz, Germany). For the synthesis of AC-Cys and AC-AET, 1 mL HCl aq. (1 mol·L^{-1}) was added before the mixture was stirred under UV-radiation.

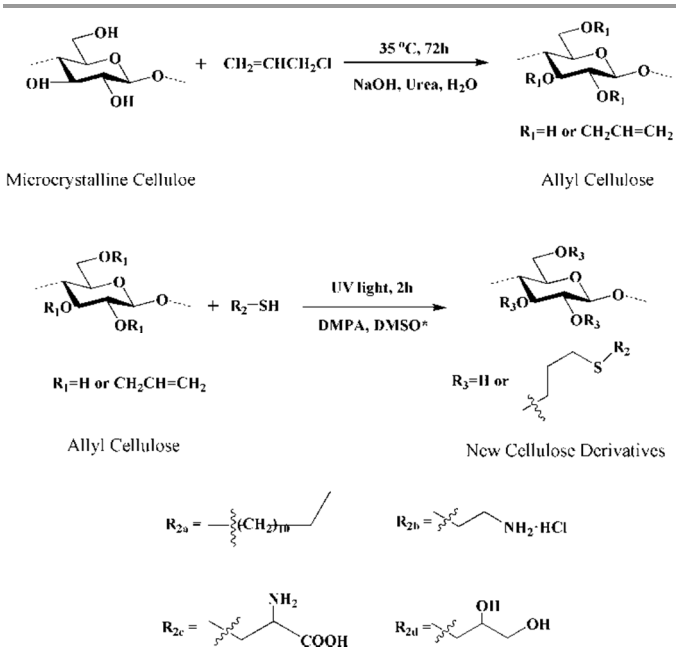
2.4. Characterization

The solubility of the samples was measured in different solvents at 25 °C with the concentration approximately 1%. FTIR spectra were performed with a Nicolet 170SX Fourier transform infrared spectrometer. The test specimens were prepared by the KBr-disk method. NMR measurements of the samples in specific deuterated solvent at 65 °C were carried on a Mercury-300BB spectrometer (^{1}H frequency =300.08 MHz, ^{13}C frequency =75.46 MHz) in the proton noise-decoupling mode with a standard 5 mm probe. The sample concentration was approximately 10 wt%. The chemical shifts were referenced to the signals of solvent and tetramethylsilane (TMS). The elemental analysis was measured with an elemental analyzer (CHNS elemental analyzer, Vario EL cube, Elementar, Germany). DS of AC (DS_{AC}) was determined through indirect iodimetry, DS of the AC-click ($DS_{AC\text{-click}}$) samples were calculated from ^{1}H NMR (AC-NDM) and the sulfur content (AC-AET, AC-Cys and AC-MG) as follows:

$$DS_{AC\text{-click}} = \frac{(161 + DS_{AC} \times 40) \times S\%}{3200 - S\% \times (M_{thiol} - 1)}$$

Where, M_{thiol} is the molar mass of the thiol compounds that were clicked to AC, S% is the sulfur content of AC-click samples.

Size exclusion chromatography (SEC) combined with laser light scattering (LLS), was used to determine the molecular weight of AC.SEC-LLS measurements were performed on a multi-angle laser light scattering instrument (DAWN EOS) equipped with a He-Ne laser (λ=632.8 nm), and combined with a pump p100 equipped with Waters Styragel HR3 and an Optilab refractometer (Waters 2410) at 25 °C. The eluent was DMF at a flow rate of 0.3 mL·min^{-1}. The specific refractive-index increment (dn/dc) of AC in DMF was 0.058 cm^3·g^{-1}, as determined by using an Optilab refractometer. Astra software was used for data acquisition and analysis.



Scheme 1. Allylation of cellulose in NaOH/urea aqueous solutions and thiol-ene reaction between AC and various thiol compounds: (a) *n*-dodecyl mercaptan (NDM); (b) 2-aminoethanethiol hydrochloride (AET); (c) cysteine (Cys); (d) monothioglycerol (MG).
*1 mL 1 mol·L^{-1} HCl was needed when the reactant was AET or Cys.

3. Results and discussion

3.1. Synthesis and structure analysis of AC

Scheme 1 illustrates the synthesis of AC, and the reaction conditions are listed in Table 1. Allyl chloride could react directly with cellulose in NaOH/urea aqueous solution without addition of an extra catalyst attributing to the basicity of the solvent. The reaction was conducted at 35 °C as the cellulose solution had a tendency to gel at higher temperature. Allyl chloride was added dropwise, while the whole mixture was stirred under the exclusion of light in order to protect the double bond from cross-linking. The reaction started homogeneously, and a clear and transparent solution was observed during the first 12 h. With the allyl group introduced onto the backbone of cellulose, the hydrophobicity of the polymer was enhanced and the mixture started to emulsify. The mixture gradually turned milky over the next 12 h and came to a white mixture. With

Table 1. Results of the allylation of cellulose in NaOH/urea aqueous solutions at 35 °C.

Sample	Molar ratio[a]	Yield	DS[b]	M_w (×10^5 g·mol^{-1})	M_n (×10^4 g·mol^{-1})	d (M_w/M_n)	Solubility[c]					
							H_2O	DMF	DMAc	DMSO	THF	$CHCl_3$
AC-1	9	83	0.98	1.34	3.19	4.2	-	+	+	+	-	-
AC-2	12	83	1.09	2.21	3.42	6.5	-	+	+	+	-	-
AC-3	18	78	1.32	2.06	4.48	4.6	-	+	+	+	-	-
AC-4	24	81	1.65	2.66	10.2	2.6	-	+	+	+	-	-

[a]Molar ratio of allyl chloride and AGU of cellulose; [b]Calculated by indirect iodimetry; [c]Soluble (+), insoluble (-).

increasing the DS of allyl groups, water solubility of the product decreased. Final white powder-like precipitates were obtained after 48 h, which could be easy isolated and purified with a high yield of approximately 80%.

As listed in Table 1, the DS of AC increased from 0.98 to 1.65, with increasing molar ratio of allyl chloride to AGU of cellulose from 9:1 to 24:1. The reaction turned heterogeneously after an amount of allyl groups introduced onto cellulose backbone. It facilitated the purification of the products but restricted the DS of AC from growing up. All the ACs could be well dissolved in DMF, DMAc and DMSO at a high concentration (over 15% w/v). The weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the polydispersity index (d) of AC were determined with SEC-LLS, and the results are also summarized in Table 1. The high d value of AC suggested that AC might be crosslinking and branching by chain transfer mechanisms in the presence of air.[23] The M_n of AC was with respect to the initial DP of the starting cellulose, indicating that the polymer degradation during etherification and purification is comparatively low. The M_n of AC-4 was high, indicating that remarkable aggregation occurred.[25]

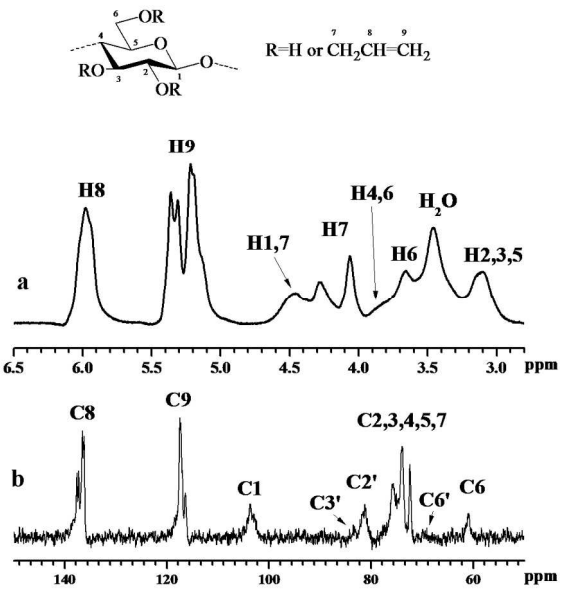


Fig. 1 (a) ^{1}H and (b) ^{13}C NMR spectra of AC-4 (DS=1.65) in DMSO-d_6 at 65 °C.

^{1}H and ^{13}C NMR spectra of AC-4 in DMSO-d_6 at 65 °C are shown in Fig. 1 (^{1}H and ^{13}C NMR spectra of AC-1~3 are displayed in Fig. S1 and S2 in the ESI), and the peak assignments are labelled according to previous work.[25] In the ^{1}H NMR spectrum, chemical shifts at 4.95-5.35 and 5.9 ppm are assigned to the H9 and H8. The chemical shift range from 4.0 to 4.5 ppm is assigned to H7. At 4.4 ppm, the signals of H1 and H7 were overlapped. The rest of hydrogen atoms present in the polymer backbone are determined between 3.0 and 3.8 ppm. In the ^{13}C NMR spectrum, the peaks at 135 and 115-117 ppm are assigned to the carbon signals of –C=C, which are determined as C8 and C9. Signals at 73.4 ppm are assigned to the C7. The peak at 102.8 ppm corresponds to C1, while the peak at 60.2 ppm is assigned to the pendant methylene carbon (C6). The rest of the carbon atoms present in the polymer backbone are determined between 70 and 85 ppm. The results demonstrated the successful synthesis of AC in NaOH/urea aqueous solutions.

3.2. Thiol-eneclick reaction of AC

In order to evaluate the capability of click-reaction of AC, four thiol compounds (NDM, AET, Cys and MG) were chosen to synthesize different kinds of cellulose derivatives (hydrophobic derivatives, polyelectrolytes, polyampholytes). All the reactions between AC and thiol reactant were performed following the procedure described in Scheme 1. As listed in Table 2, the reaction was heterogeneous when the thiol reactant was NDM or Cys, and was homogeneous when the reactant was AET or MG. All the products could be dissolved in the chosen solvent at a high concentration (more than 10% w/v). AC-NDM could only be dissolved in pyridine owing to its long carbon chain. AC-MG could only be dissolved in DMSO. AC-AET and AC-Cys displayed good solubility in HCl aq. (1 mol·L^{-1}) and DMSO/HCl solution (20/3 v/v, 1 mol·L^{-1} HCl aq.). AC-Cys could be dissolved in NaOH aq. (1 mol·L^{-1}) as it contains both cation and anion ions, while AC-AET could not be dissolved due to its numerous cation ions.

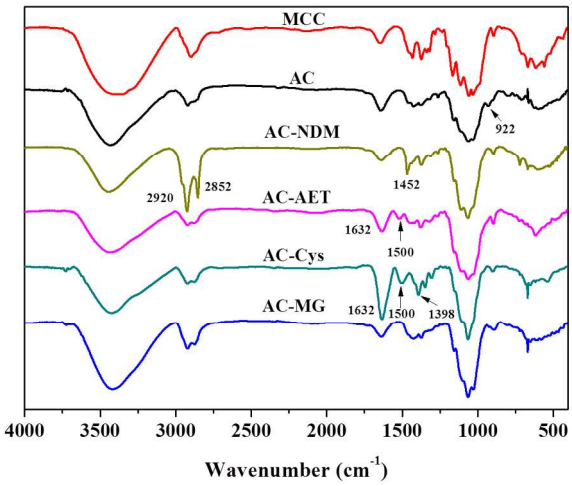


Fig. 2 FTIR spectra of MCC, ACand the AC-click samples (AC-NDM, AC-AET, AC-Cys and AC-MG).

Fig. 2 shows the FT-IR spectra of AC-4 and its clicked products. For AC-4, the presence of –C=C group is indicated by the peak at 922 cm^{-1}. The peaks at 2920, 2852 and 1452 cm^{-1} for AC-NDM

Table 2. Reaction and solubility of the AC-thiol click products

Sample	Reaction		Solubility[a]					
	Type	Product	DMSO	DMSO/HCl/H_2O	Pyridine	H_2O	NaOH aq.	HCl aq.
AC	/	/	+	-	-	-	-	-
AC-NDM	Heterogeneous (L/L)	Precipitation	-	-	+	-	-	-
AC-AET	Homogeneous	Solution	○	+	-	○	-	+
AC-Cys	Heterogeneous (S/L)	Solution	○	+	-	○	+	+
AC-MG	Homogeneous	Solution	+	-	-	-	-	-

[a]Soluble (+), insoluble (-), swelling (○).

represent the asymmetrical, symmetrical stretching and bending vibration of methylene, respectively. For AC-AET, a signal of -NH_2 was observed at 1500 and 1632 cm^{-1}. For AC-Cys, the presence of -COO^- groups was indicated by the peaks at 1398 and 1632 cm^{-1}, while the presence of –NH_2 groups was indicated by the peaks at 1500 and 1632 cm^{-1}. The spectrum of AC-MG was similar to MCC due to the strong similarities in their functional groups.

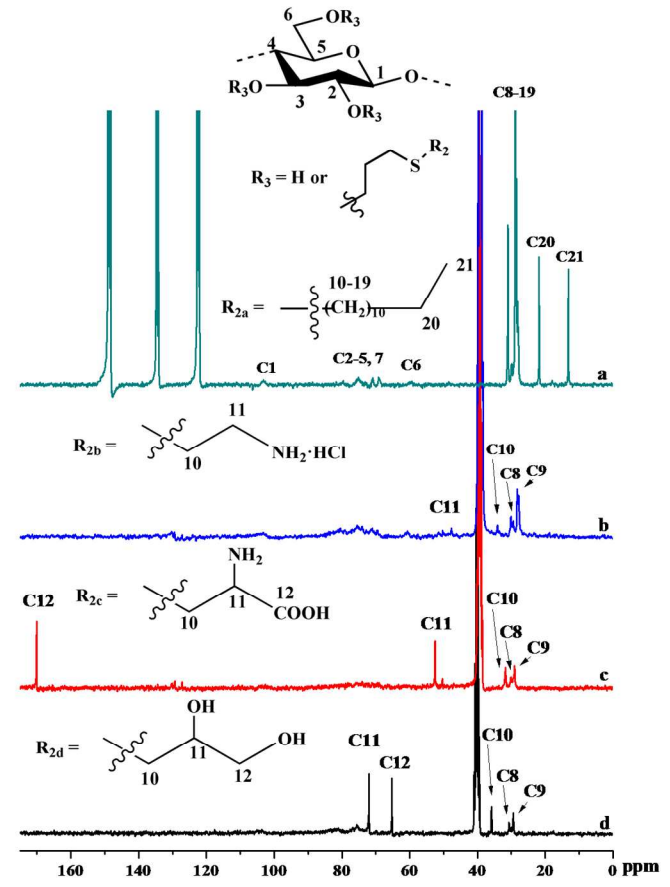


Fig. 3 ^{13}C NMR spectra of (a) AC-NDM in deuterated pyridine, (b) AC-AET in HCl/H_2O/DMSO-d_6 (1 mol·L^{-1} HCl aq., 3/20 v/v), (c) AC-Cys in HCl/H_2O/DMSO-d_6 (1 mol·L^{-1} HCl aq., 3/20 v/v) and (d) AC-MG in DMSO-d_6.

Fig.3 displays the ^{13}C NMR spectra of the AC-click samples, and the peaks are assigned as follows.[34-37]

AC-NDM: δ (ppm) = 103.2 (C1, AGU), 60.0–79.8 (C2–C5, AGU; C7), 60.2 (C6, AGU), 28.1-31.0 (C8-C19), 21.8 (C20), 13.2 (C21).

AC-AET: δ (ppm) = 103.2 (C1, AGU), 60.0–79.8 (C2–C5, AGU; C7), 60.2 (C6, AGU), 47.7-50.3 (C11), 34.1 (C10), 29.4-30.1 (C8), 27.8-28.3 (C9).

AC-Cys: δ (ppm) = 170.1 (C12), 103.2 (C1, AGU), 60.0–79.8 (C2–C5, AGU; C7), 60.2 (C6, AGU), 50.3-52.6 (C11), 31.8 (C10), 30.1 (C8), 29.0 (C9).

AC-MG: δ (ppm) = 103.2 (C1, AGU), 60.0–79.8 (C2–C5, AGU; C7), 72.0 (C11), 65.2 (C12), 60.2 (C6, AGU), 35.9 (C10), 30.7 (C8), 29.4 (C9).

The chemical shifts at 135 and 115-117 ppm, which are assigned to the carbon signals of –C=C, cannot be found in the spectra of all the AC-click products. The result demonstrated that the allyl groups were completely reacted. The DS values of AC-click products were calculated and listed in Table 3, a high conversion was obtained with few side reactions. The conversion of AC-1-AET was about 70%, AC-1-Cys was over 80%, while AC-1-NDM and AC-1-MG were around 90% or more, respectively.

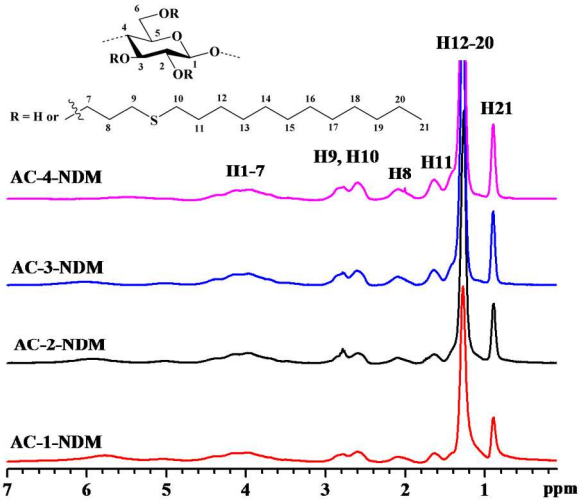


Fig. 4 ^{1}H NMR spectra of AC-NDM samples in deuterated pyridine.

To explore the influence of the derivation degree of allyl groups on the click reaction, an excess amount of NDM was reacted with AC at different DS value. Fig. 4 shows the ^{1}H NMR spectra of AC-

Table 3. Conditions and results of the thiol-ene click reaction of different thiol containing reagents with AC

Sample	AC	Reagent		Product		
	DS_{AC}	Thiol compound	Molar ratio[a]	Sulfur content (%)	$DS_{AC\text{-}click}$[b]	Conversion (%)
AC-1-Cys	0.98	Cys	1.6	7.81	0.80	82[c]
AC-1-AET	0.98	AET	1.6	7.80	0.68	69[c]
AC-1-NDM	0.98	NDM	1.6	/	0.88	90[c]
AC-2-NDM	1.09	NDM	1.6	/	1.01	93[c]
AC-3-NDM	1.33	NDM	1.6	/	1.15	86[c]
AC-4-NDM	1.65	NDM	1.6	/	1.64	99[c]
AC-1-MG-1	0.98	MG	0.4	3.97	0.29	75[d]
AC-1-MG-2	0.98	MG	0.8	7.48	0.63	81[d]
AC-1-MG-3	0.98	MG	1.2	9.33	0.85	73[d]
AC-1-MG-4	0.98	MG	1.6	9.47	0.87	89[c]

[a]Mol reagent per mol repeating unit of AC;
[b]DS of AC-NDM samples determined by ^{1}H NMR; AC-Cys, AC-AET and AC-MG samples calculated by sulfur content (*S*%);
[c]Conversion (%) = $DS_{AC\text{-}click}/DS_{AC}$;
[d]Conversion (%) = $DS_{AC\text{-}click}/(DS_{AC}\cdot MR_{MG})$, MR_{MG} is the molar ratio of MG to the repeating unit of AC.

NDM samples. The peak intensity of methyl groups (H21, δ=0.88 ppm) was found to become stronger with an increase of the DS of AC and AC-NDM samples. The DS of the samples were calculated from ^{1}H NMR (Table 3). All the AC samples have a relatively high conversion at around 90% despite of their DS values. The result illustrated that the structure of the final products could be easily manipulated by changing the DS of AC.

The DS of the final products could also be controlled by regulating the amount of thiol reactant. As shown in Table 3, with the amount of MG increasing, the DS of the AC-click product increased when the molar ratio of MG and unit of AC was less than 1.2. When the molar ratio was 1.2 or more, the DS of the AC-click products remained unchanged because all the allyl groups were completely reacted. MG had a high conversion rate of around 80% when the allyl groups were sufficient. As displayed in Fig. 5, the carbon signals of –C=C could still be found in the ^{13}C NMR spectrum of AC-1-MG-1, indicating that the product could continue to react with other thiol compounds. This makes it possible to synthesize cellulose derivatives, which contains different functional groups, quantitatively and step by step.

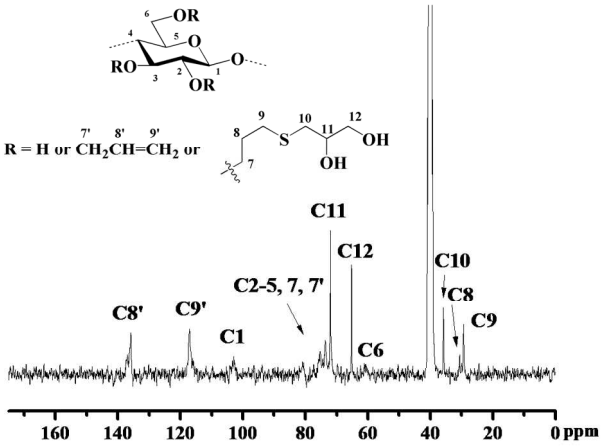


Fig. 5 ^{13}C NMR spectrum of AC-1-MG-1 in DMSO-d_6 at 65 °C.

4. Conclusions

AC samples were successfully synthesized in NaOH/urea aqueous solutions under moderate conditions. The reaction began homogeneously but ended heterogeneously, which provided the AC with a high DS and facilitated its purification. The total DS of the AC increased from 0.98 to 1.65 with increasing molar ratio of allyl chloride to AGU from 9:1 to 24:1. All the AC samples showed a high solubility in organic solvents such as DMSO, DMAc and DMF. The thiol-ene click reaction of AC provided a simple, quick and mild route to a wide variety of selectively functionalized products. NDM, AET, Cys and MG were chosen as thiol reactants and different kinds of cellulose derivatives were successfully synthesized. The conversions of both thiol and AC succeeded with few side reactions and yielded pure derivatives. This process provides a novel broad stage for the mild and diverse derivatization of cellulose.

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Notes

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†Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR spectra of AC samples See DOI: 10.1039/b000000x/

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