Thermal Studies on Homogeneously Synthesized Cellulose p-Toluenesulfonates

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SYNOPSIS

The thermal behavior in argon of homogeneously synthesized cellulose p-toluenesulfonates (tosylates) with a degree of substitution (DS) ranging from 0.4 to 2.3 was studied by means of thermogravimetry and derivative thermogravimetry from ambient temperature up to 500°C. For comparison, the thermal behavior of the starting celluloses used (pulps, linters, bacterial cellulose) was also examined. The thermal degradation of cellulose tosylates was initiated at lower temperature than cellulose itself and proceeds in two main stages. The temperature of the first one (169–196°C) increases with increasing DS and is independent of the molecular weight. Activation energies calculated following the method of Broido, FTIR, and ultimate analysis as well as mass spectroscopy show that the first stage of degradation is closely associated not only with the scission of tosyl ester groups but also with a partially degradation of the polymer backbone. Further, the temperature-concentration diagram for the system cellulose tosylate 20/o-dichlorobenzene was studied by optical observations and calorimetric investigations. A liquid–liquid demixing interferes with the glass transition of the cellulose tosylate–solvent system. It results in the solidification of the solution. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The naturally occurring polysaccharide cellulose formed both from plants and bacteria has been reevaluated recently as a renewable resource. Its potential to develop further as a new, functional chemical or high-performance material has been gained new impetus by the development of different synthesis paths for homogeneous phase reactions. Both the chemical modification of cellulose in non-aqueous solvents[1–3] and via instable organo-soluble intermediates[4–6] permits control of the degree of substitution (DS) in a wide range as well as the distribution of substituents. At present, one of the most common solvents for the homogeneous modification of unmodified cellulose is the system N,N-dimethyl acetamide (DMA)/LiCl first described by Mc-

Cormick.[7] It has been used for the synthesis of various cellulose esters and ethers.[8,9]

In the course of our studies on homogeneous phase reactions of cellulose[10,11] using protecting group technique and activation effects our interest was focused on cellulose p-toluenesulfonates (tosylates) as a valuable intermediate. In a previous article, the homogeneous synthesis of organo-soluble cellulose tosylates within a wide DS range from 0.4 to 2.3 in DMA/LiCl as well as both the characterization of the distribution of the substituents and the chemical stability in dependence on the total DS are described.[12]

On the other hand, heterogeneously prepared cellulose tosylates have been found to be of considerable interest due to their thermal properties.[13,14] For instance, cellulose tosylates synthesized in a slurry of cellulose in pyridine were chosen to investigate the influence of blocking groups on the thermal decomposition of cellulose.[15] Furthermore, cellulose tosylates show increased flame resistance in comparison with the starting cellulose. However, no information on the thermal behavior of homoge-

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neously synthesized cellulose tosylates as well as their dependence on the DS and on the distribution of substituents are available. The knowledge of thermal properties of cellulose derivatives is also important in connection with creating new cellulosic materials.

In this work, we studied the thermal properties of homogeneously synthesized (DMA/LiCl) cellulose tosylate samples in dependence on the DS by using thermogravimetry (TG). The thermal properties below 200°C useful for subsequent chemical reactions and processing are of special interest. Attempts were made to gain information on the mechanism of thermal degradation. Further, the thermally induced phase separation of the system cellulose tosylate/o-dichlorobenzene was investigated by differential scanning calorimetry (DSC). Such systems open up possibilities for preparing new and interesting structures.

EXPERIMENTAL

Materials

The cellulose tosylate samples 7–23 (see Table I) were prepared under homogeneous reaction condi-

tions in DMA/LiCl (4% cellulose content) using various starting cellulose materials 1–6 and p-toluenesulfonyl chloride and triethylamine as a base within 24 h at 8°C according to Rahn and colleagues.[12] The DS values determined on the basis of sulfur content are given in Table I.

Dissolution of Cellulose in N,N-Dimethyl Acetamide (DMA)/LiCl, Typical Example

Air-Dry cellulose (20.2 g) (118.7 mmol, actual weight of water-free cellulose) was suspended in 470 mL of DMA, kept at 160°C for 1 h, and stirred. In order to replace water bound to cellulose, about 40 mL of DMA were removed by distillation in nitrogen atmosphere. After the slurry had been allowed to cool to 100°C, 40 g of anhydrous LiCl were added. By cooling to room temperature and stirring, the cellulose dissolves completely within some hours.

p-Toluenesulfonylation of Cellulose, Typical Example

To the solution of 20.2 g of air-dry cellulose in DMA/LiCl (4.3%, w/w) a mixture of 59.4 mL (427.2 mmol) of triethylamine and 40.6 mL of DMA (ratio 10 : 7,

Table I Description of the Cellulose Tosylate Samples Used

Starting Cellulose Sample			Molar Ratio[b] Tos-Cl/AGU	Sample No.	Cellulose Tosylate			$[\eta]^d$ Shape (dL/g)	
No.		DP[a]			DS[c]	S (%)	Cl (%)		
1	Powder	280	1.8	7	1.36	11.69	0.47	0.73	particular
1	"Avicel"		6.0	8	2.02	13.63	0.44	—	particular
1			4.5	9	2.30	14.20	0.43	0.81	fibrous
2	Powder	330	1.8	10	1.32	11.55	0.42	0.71	particular
2			1.8	11	1.39	11.80	0.40	0.72	particular
3	Spruce	650	1.8	12	1.34	11.68	0.44	1.10	particular
3	sulfite pulp		9.0	13	1.84	13.25	0.49	—	particular
4	Linters	850	0.6	14	0.38	5.69	0.35	—	particular
4			0.9	15	0.46	6.23	0.40	2.15	fibrous
4			1.5	16	0.93	9.75	0.45	1.24	particular
4			1.8	17	1.12	10.70	0.50	1.61	particular
4			2.1	18	1.35	11.69	0.40	1.27	fibrous
4			2.4	19	1.54	12.30	0.55	1.32	particular
4			3.0	20	1.79	13.05	0.45	1.18	particular
4			3.0	21	2.04	13.74	0.50	1.39	fibrous
5	Beech sulfite pulp	1020	1.8	22	1.32	11.55	0.43	2.27	fibrous
6	Bacterial cellulose[e]		1.5	23	0.55	7.16	0.40	—	fibrous

[a] DP: Degree of polymerization determined viscometrically according to Doering[16].

[b] 0.12 mol anhydroglucose units (AGU), 4% (w/w) solution, 2 mol triethylamine/mol p-toluenesulfonyl chloride (Tos-Cl).

[c] DS: Degree of substitution calculated on the basis of sulfur analysis.

[d] Intrinsic viscosity determined in dimethyl sulfoxide at 32°C.

[e] Bacterial cellulose from *Acetobacter xylinum*,[17] course of reaction partially heterogeneous.

v/v) was added while stirring. After cooling to about 8°C and stirring, a solution of 40.7 g (213.6 mmol) p-toluenesulfonyl chloride in 60 mL DMA (see Table I) was dropwisely added within 30 min. The homogeneous reaction mixture was stirred for 24 h at 8°C, and then slowly poured into 5 L of ice water. The precipitate was filtrated off, carefully washed with about 15 L of distilled water and 2 L of ethanol, suspended in 1 L of acetone, and reprecipitated into 3 L of distilled water. After filtration and washing with ethanol, the sample was dried at 50°C under vacuum (7).

Yield: 75 %, degree of substitution (DS) = 1.36 (based on sulfur analysis), intrinsic viscosity $[\eta]$ 0.73 dL/g (Table I).

FTIR (KBr): 3523 (ν OH), 3072 (ν C — H$_{arom.}$), 2891 (ν CH), 1598, 1500, 1453 (ν C — C$_{arom.}$), 1364 (ν_{as} SO$_2$), 1177 (ν_s SO$_2$), 814 (δ C — H$_{arom.}$) cm^{-1}; see also Figure 7, spectrum a.

^{13}C NMR (DMSO-d_6): δ 144.7–127.4 (tosylate aromatics), δ 105–65 (cellulose backbone), 20.7 (CH$_3$) ppm.

Measurements

The degree of polymerization (DP) of the starting cellulose samples was determined by a viscometric method.[16]

Intrinsic viscosities in DMSO solution were determined with an Ostwald viscometer (Schott AG, Mainz) at 32°C.

The thermogravimetric, derivative thermogravimetric, and scanning calorimetric analysis were performed by means of a Setaram TGDSC 111 analyzer using 10 mg samples. The thermograms were run under argon flow (20 mL/min.) at a heating rate of 5 K/min from ambient temperature up to 500°C.

The FTIR spectra were recorded on a Nicolet Impact 400 spectrometer using KBr pellets.

^{13}C NMR spectra were acquired on a Bruker AMX 400 spectrometer; the accumulation number was between 10,000–15,000 scans.

Wide-angle x-ray scattering (WAXS) diagrams were measured at room temperature on a Rigaku Rotaflex RU-200B rotating anode (12 kW) equipped with a horizontal Bragg-Brentano focusing diffractometer and scintillation counter. The scattering patterns were recorded (40 kV, 100 mA) in the transmission mode, employing Ni-filtered CuKα radiation (λ = 1.5418 Å) as a function of the scattering angle 2Θ from 5 to 60° with a step size of 0.05° (2Θ) and a measuring time of 10 s per step.

Samples for optical observations were prepared by dissolving the appropriate amount of cellulose tosylate **20** in o-dichlorobenzene in sealed glass tubes. They were cooled at 0.5 K/min. The onset of opalescence was recorded by the naked eye.

Calorimetric observations were performed at a scanning rate of 10 K/min with a Perkin–Elmer DSC-7 equipped with a thermal analysis data station. Samples were prepared directly in the DSC sample pans and were homogenized for 48 h at 40°C and 0.5 h at 140°C.

RESULTS AND DISCUSSION

The homogeneous tosylation of cellulose dissolved in DMA/LiCl represents a suitable and effective method for the preparation of cellulose tosylates with an insignificant incorporation of chlorodeoxy functions.[12] The degree of substitution (DS) can be simply controlled by the molar ratio of tosyl chloride/anhydroglucose unit. As confirmed by ^{13}C NMR spectroscopy as well as by analysis of corresponding iododeoxy cellulose tosylates, the tosylation at the O-6 atom is more effective than those at the O-2/3 atoms.[12]

Thermogravimetry of Cellulose p-Toluenesulfonates (Tosylates)

Thermal analysis of cellulose (**1–6**, see Table I) and homogeneously synthesized cellulose tosylates (**7–23**) were carried out under argon atmosphere from ambient temperature to 500°C.

A representative thermogravimetric (TG) curve of starting cellulose **4** (Fig. 1) and the cellulose tosylate **17** (Fig. 2) obtained by esterification in N,N-dimethyl acetamide (DMA)/LiCl under homogeneous reaction conditions showing that the thermal degradation of the cellulose tosylate sample was initiated at a lower temperature than cellulose itself. The degradation of cellulose starts at 260°C and exhibits one-stage pyrolysis (main weight loss) leaving only 30% char at 460°C. In some cases, the initial but small weight loss below 100°C is due to the evaporation of moisture and was neglected. On the other hand, the TG curve of the cellulose tosylates can be subdivided into two parts. There is almost no weight loss below 100°C associated with the evaporation of moisture. This is reasonable as the moisture-absorbing capacity of the cellulose tosylates decreases when the moisture-holding hydroxyl groups are substituted by ester groups. For sample **17** with a DS of 1.12, the first part starts at 160.0°C and ends at 181.2°C, and represents a weight loss of 13.7% in a narrow temperature range. The second
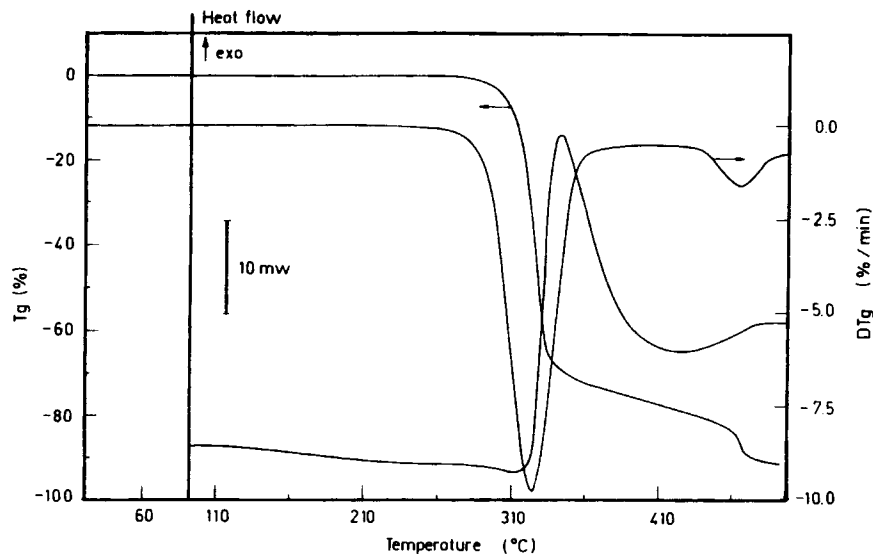
Figure 1   Thermal analysis of cellulose **4** (see Table I) under argon atmosphere.

part, ranging from 181.3°C to 265.5°C represents a weight loss of 29.4%. The further heating of the sample up to 500°C leads to carbonization of the products to ash. The values obtained for all samples are summarized in Table II.

To compare the thermal stability of cellulose to-sylates with different DS we used samples synthesized starting from the same cellulose (**4,** DP 850). The different DS was adjusted by the molar ratio of cellulose to p-toluenesulfonyl chloride, for instance, the samples have an identical chemical "history." In Figure 3, the decomposition temperatures of two main stages in a DS range from 0.38 to 2.04 (samples

14–21) are shown using the inflection point temperature of the corresponding DTG curve (super-imposed upon the TG curve in Fig. 2). The temperature of the first degradation stage increases (162–182°C), and that of the second one decreases with increasing DS.

It is known that the rate of pyrolysis of cellulose is inversely proportional to the square root of DP. The cellulose samples **1–5** show a slight increase in their thermal stability with increasing DP ranging from 280 to 1020 (Fig. 4). On the other hand, cellulose tosylates (**7,10,11,18,22**) with equal DS of 1.32–1.39 but different intrinsic viscosities, corre-
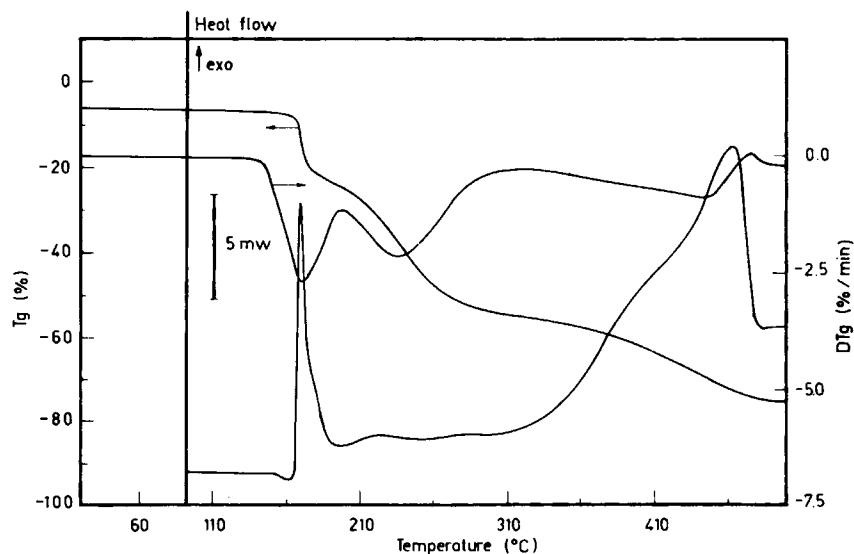

Figure 2   Thermal analysis of cellulose tosylate **17** (see Table I) under argon atmosphere.

Table II Thermogravimetric Analysis of Cellulose Tosylates

Sample No.	DS	IDT-1[a] (°C)	FDT-1[b] (°C)	Heat Flow (mJ/mg)	Weight Loss-1 (%)	IDT-2[a] (°C)	FDT-2[b] (°C)	Weight Loss-2 (%)	Residue at 460°C (%)
7	1.36	169.1	180.0	307.8	10.3	180.1	257.3	31.8	36.5
8	2.02	176.4	189.1	312.6	9.7	176.5	254.5	31.4	38.3
9	2.30	186.1	195.9	365.8	10.0	196.0	264.6	37.7	33.1
10	1.32	169.1	186.1	324.2	13.5	186.2	259.1	27.1	27.6
11	1.39	170.0	182.7	308.4	11.2	182.8	260.0	31.8	38.8
12	1.34	169.1	183.6	309.7	11.8	183.7	256.4	29.4	37.1
13	1.84	176.4	187.3	331.2	9.1	176.5	260.9	32.6	38.3
14	0.38	155.4	169.1	200.4	21.2	169.2	309.9	22.9	29.4
15	0.46	150.7	174.5	380.3	21.8	174.6	307.3	35.7	29.7
16	0.93	158.2	172.2	372.3	15.4	172.3	280.2	33.7	29.1
17	1.12	160.0	181.2	348.9	13.7	181.3	265.5	29.4	27.5
18	1.35	165.4	180.9	339.0	12.3	181.0	261.2	32.8	36.6
19	1.54	176.4	187.3	327.0	10.3	187.4	263.6	33.7	23.7
20	1.79	180.0	190.1	337.6	8.9	190.2	244.9	30.3	26.8
21	2.04	179.6	191.8	310.9	8.8	191.9	260.0	32.3	31.2
22	1.32	167.3	180.0	310.3	10.6	180.1	260.0	29.4	32.3
23[c]	0.55	170.0	183.4	301.6	18.0	183.5	289.6	37.7	32.3

[a] Initial decomposition temperature.
[b] Final decomposition temperature.
[c] Bacterial cellulose, course of reaction partially heterogeneous.

sponding to different DP, exhibit almost the same degradation temperature for both degradation steps (Fig. 4).

In addition to plants, bacteria such as *Acetobacter xylinum* are able to produce extracellularely cellulose of high purity and crystallinity as well as high water absorption capacity and mechanical strength in the wet state.[17] Because of these features, we were interested in selected properties and in the reaction behavior of bacterial cellulose (BC).[18] In this work a cellulose tosylate **23** with a DS of 0.55 starting
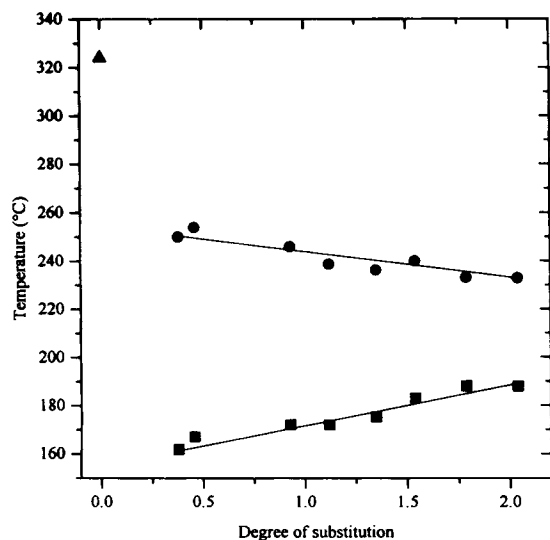

Figure 3 Peak temperature of the first (■) and second (●) degradation stage of cellulose tosylates **14–21** (see Table I) as a function of the degree of substitution. The degradation of cellulose **4** (▲) is added for comparison.
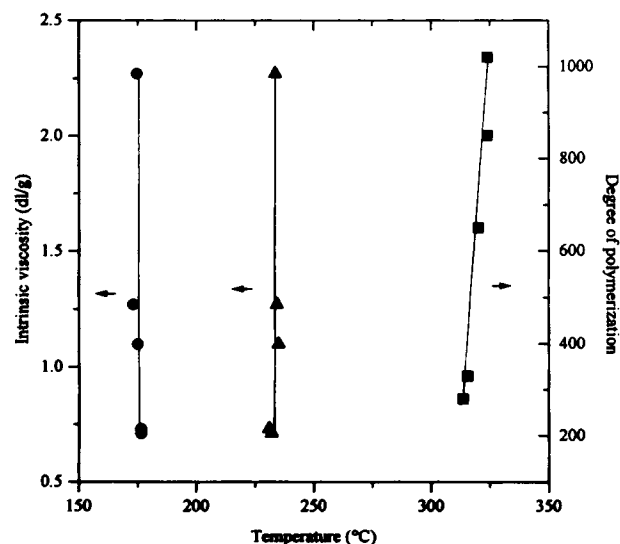

Figure 4 Degradation temperature of cellulose 1–5 (■, see Table I) and cellulose tosylates **7,10,12,18,22** (● first and second stage of degradation, see Table I) as a function of the molecular weight; (curves are drawn by hand).

from solvent-exchanged BC **6** using 1.5 mol tosyl chloride per mol anhydroglucose unit was synthesized. The relatively low DS in comparison with plant celluloses might be result from a partially heterogeneous course of reaction. From the viewpoint of the thermal behavior (Table II), the sample **23** exhibits the same properties as a cellulose tosylates prepared from plant cellulose, for instance, the degradation occurs in two main stages, while the degradation temperature of the starting BC is strongly influenced by the purification treatment as illustrated by Geyer and colleagues.[18] The degradation, however, starts at a significantly higher temperature compared to a cellulose tosylate obtained from plant cellulose with the same DS, probably due to a partially heterogeneous course of reaction and thereby a remaining degree of order.

The values obtained show that the cellulose tosylates are as stable as heterogeneously prepared samples[13-15] and less stable than the starting cellulose. This may be explained by the fact that the main source of thermal stability is the crystalline order caused by hydrogen bonds. In less ordered cellulose derivatives, the hydrogen bond concentration is correspondingly less.[19] Preliminary x-ray investigations indicate that in comparison with the starting cellulose of a crystal modification I, low substituted cellulose tosylates are amorphous. Typical x-ray pattern are shown in Figure 5(a) and (b). On the other hand, with increasing DS of tosyl groups, an increase in supramolecular order was observed. Therefore, the increase in temperature of the first degradation stage may be explained in recovering some degree of order owing to the increase in its regularity [Fig. 5(c)].

In the temperature range of the first degradation stage all samples **7–23** investigated show a sharp distinct exothermic signal, which starts with a very small endothermic region (compare Fig. 2). The integration of the exothermic peaks yields a heat flow in the range from 301.6 to 380.2 mJ/mg except for sample **14** with a low DS of 0.38 (Table II). This behavior gives rise to the assumption that the initiation of degradation of cellulose tosylates is always the same, independent of the DS values.

Studies on the Mechanism of Thermal Degradation

In order to gain information on the mechanism of thermal degradation, the activation energies of the first stage of degradation were determined according to the Broido method.[20] The method uses the equation
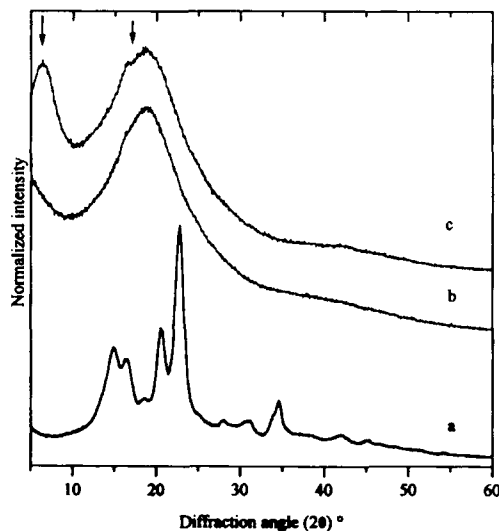

Figure 5 X-ray diffraction pattern (a) of cellulose **4**, and (b, c) of cellulose tosylates **15** and **21**, respectively (see Table I).

$$\ln \ln (1/y) = -(E/R)(1/T) + \text{const.}$$

The residual fraction (y) is defined as

$$y = 1 - \frac{w_o - w_r}{w_o - r} = 1 - \frac{w}{w_o - r}$$

where w_r = weight of sample remaining at time t, w_o = initial weight, w = weight loss at time t, r = inactive residue.

Plots of $\ln \ln (1/y)$ vs. $1/T$ for some cellulose tosylates are given in Figure 6. It can be seen that cellulose tosylate sample **16** with a comparable low DS shows a straight line that corresponds to an activation energy of 518.6 kJ/mol. For samples with a higher DS two different sections with different slope appear that can be attributed to the presence of two decomposition mechanisms. Such a behavior appears at a DS of 0.93. The values of activation energies, E_a and for the activation energy reduced by the molecular mass of the repeating unit, $E_{a,red}$ are given in Table III. The E_a increases from 507.3 to 732.5 kJ/mol for the first stage of degradation. The corresponding reduced value $E_{a,red}$ is almost invariant in the DS range investigated (1.357–1.697 kJ/g). This points to the same degradation mechanism of all samples. The $E_{a,red}$ values of the second slope are more dependent on DS, for instance, the degradation path might be determined by the number of substituents. The very high E_a value for sample **14**, which is in comparison with all other sam-
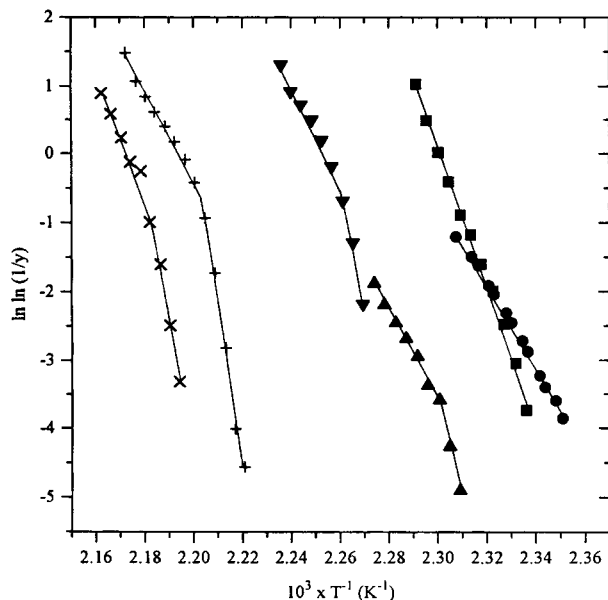
Figure 6 Plots of ln ln $(1/y)$ vs. $1/T$ of cellulose tosylates using the Broido method. (●) **14**, (■) **15**, (▲) **16**, (▼) **18**, (+) **19**, (×) **20**; (curves are drawn by hand).

Figure 7 FTIR spectra of cellulose tosylate **20** before (a) and after (b) a thermal treatment up to 190°C.

ples not soluble in any solvent, cannot be explained with the present results.

Figure 7 shows representative FTIR spectra of the cellulose tosylate (sample **20**) before (spectrum a) and after a thermal treatment up to 190°C (spectrum b), for instance, the temperature of the first degradation stage. These spectra show the characteristics of the cellulose backbone. Furthermore, signals at 1364 and 1177 cm^{-1} can be observed indicating the presence of tosyl ester groups. The thermal treatment of cellulose tosylates yields a sig-
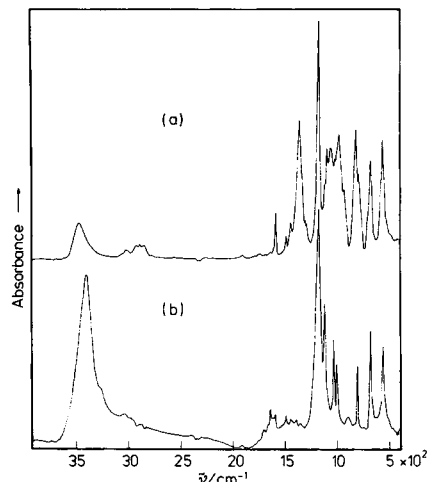
nificant change in the molecular structure. In the FTIR spectra, the typical signals for the cellulose tosylate ester bonds disappear and the characteristic peaks of the cellulose backbone cannot be clearly seen. In the OH region, a band at 3408 cm^{-1} with high intensity occurs. The spectrum is quite similar to that of p-toluenesulfonic acid. The ultimate analysis of the residue gave a sulfur content of 12.84% (the value of the untreated sample **20** is 13.05%). As revealed by means of mass spectroscopy (chemical ionization) the cellulose tosylates contain no free p-toluenesulfonic acid. After the thermal treatment at 190°C, an abundant fragment at m/z 173 appears in the mass spectrum indicating the production of p-toluenesulfonic acid.

Table III   Activation Energies for the First Stage of Thermal Degradation of Cellulose Tosylates

Sample No.	DS	Temperature (°C)	E_a (kJ/mol)	M[a] (g/mol)	E_a/M (kJ/g)
14	0.38	154.1–163.7	827.6	220.73	3.749
15	0.46	150.1–163.2	507.3	233.07	2.177
16	0.93	159.0–171.7	518.6	305.53	1.697
			1280.5		4.191
17	1.12	166.6–174.5	524.1	334.83	1.565
			1280.5		3.834
19	1.54	175.8–187.6	542.1	399.59	1.357
			1953.2		4.888
20	1.79	180.0–190.6	714.1	438.13	1.630
			1593.6		3.637
21	2.04	168.3–187.7	732.5	437.60	1.674
			1294.3		2.958

[a] Molecular mass of the repeating unit.

The decreasing in weight loss for the first degradation stage with increasing DS (Table II, compare samples **14–21**) indicates that volatile degradation products of the polymer chain are mainly formed at lower DS values because p-toluenesulfonic acid itself does not decompose and evaporate at temperatures below 210°C.

Summarizing these results, it may be concluded that the first degradation stage is closely associated with the scission of tosyl groups from the cellulose tosylate. This was assumed for heterogeneously prepared cellulose tosylates, too.[13,14] However, the formation of the p-toluenesulfonic acid in a water-free inert atmosphere leads to rapid protonation of the glycosidic oxygen atom with consequent fission of the glycosidic bond, for instance, the cellulose chains are depolymerized. This assumption agrees with the finding of two slopes of E_a for cellulose tosylates with DS > 0.93. The increase in the amount of released acid, a strong dehydrating agent, with increasing DS may explain the slight decrease in temperature for the second stage of degradation.

Solution Behavior of Cellulose Tosylate

The cellulose tosylates synthesized are soluble in different organic solvents like, for example, N,N-dimethylformamide, N,N-dimethyl acetamide, and dimethyl sulfoxide at room temperature.[12] On the other hand, we have found that sample **20** is soluble in o-dichlorobenzene at higher temperature and solidifies on cooling. In order to gain quantitative information of this interesting system the thermal
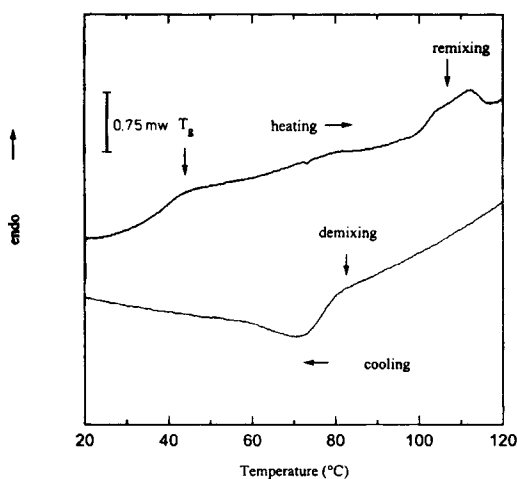

Figure 8 Calorimetric observation of liquid–liquid demixing (cooling) and T_g and remixing (heating) by differential scanning calorimetry (DSC) for the system cellulose tosylate **20**/o-dichlorobenzene (ϕ_2 = 0.19).
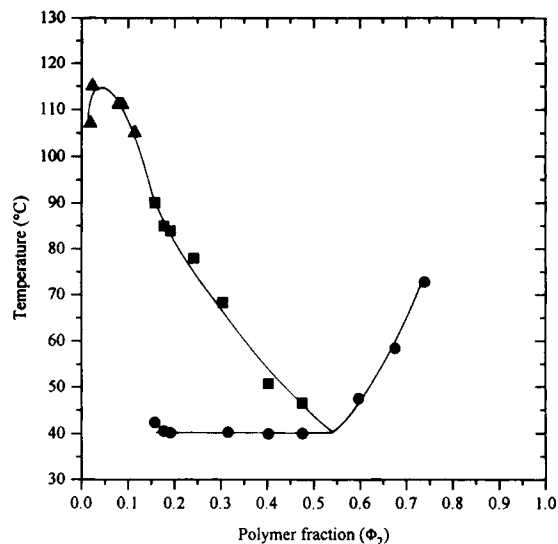

Figure 9 Temperature–concentration diagram for the system cellulose tosylate **20**/o-dichlorobenzene: T_{op} (▲); T_d (■); T_g (●); (curves drawn by hand).

transitions that can take place are studied by optical and calorimetric techniques.[22,23] The flocculation temperature, T_{op}, is obtained from optical observations. This technique is generally used in the low concentration region (polymer weight fraction ϕ_2 < 0.10). At higher concentrations, important difficulties are encountered in the preparation of the samples and the liquid–liquid demixing is generally studied by calorimetry. Small, easier preparable samples can be used.

On cooling a solution in the differential scanning calorimeter, an exothermic signal is observed. A typical example is represented in Figure 8. The temperature at the onset of this peak is taken as the demixing temperature T_d. It agrees quite well with the optically determined T_{op}. Both temperatures are used to construct the demixing curve in the temperature–cellulose tosylate concentration phase diagram. This is presented in Figure 9. No demixing is observed at cellulose tosylate concentrations ϕ_2 > 0.52. Calorimetry reveals only a glass transition, T_g. Its value increases with increasing cellulose tosylate content. At cellulose tosylate concentrations ϕ_2 > 0.75 significant problems exist to reveal the T_g temperature. This is probably due to the moisture absorbing capacity of cellulose derivatives having substantial amounts of unmodified hydroxyl groups, as already discussed by Glasser.[24] At cellulose tosylate concentrations in the region of phase separation, a concentration-independent T_g is expected.[25]

The intersection point of T_g vs. ϕ_2 curve and the demixing curve is situated at + 40°C and ϕ_2 = 0.53.

The constant value of T_g in the demixing region results from the interference between L–L demixing and glass transition. Domains of high cellulose tosylate concentrations are in equilibrium with domains of low cellulose tosylate concentrations. The cellulose tosylate concentration in the former ones is not influenced by the initial concentration. They vitrify when the temperature of the intersection of the demixing curve and the T_g vs. ϕ_2 curve is reached.[25]

While x-ray diffraction pattern of solutions of the tosyl cellulose sample **20** exhibit only the broad signal between 20 and 35° indicating that no supramolecular order exists, the dimixed system shows an additional sharp peak near 10° (Fig. 10). Therefore, a certain degree of regularity is introduced by the demixing process.

CONCLUSIONS

The thermal stability of homogeneously synthesized organo-soluble cellulose tosylates depends on the DS of the tosyl groups. With increasing content of the tosyl groups (DS 0.38–2.30) an increase in stability from 169 to 196°C occurs. The supramolecular structure of the cellulose tosylates derives from the hydrogen bond network established between the cellulose hydroxyls and the tosyl groups, which obviously leads to a formation of a new supramolecular order of samples with higher DS and thereby to an increase in thermal stability. The molecular weight, on the other hand, does not influence the degradation temperature at comparable DS. The stability is sufficiently high for processing and subsequent chemical modifications. However, in order to avoid thermally induced side reactions the different processes should be carried out below 160°C. The onset of degradation is closely associated not only with the scission of tosyl groups from the cellulose tosylate but also with a partial degradation of the polymer backbone.

Moderately concentrated solutions of cellulose tosylate **20** in o-dichlorobenzene solidify when they are cooled to temperatures below 40°C. This result from an interference of L–L demixing and T_g.

The supramolecular structure as well as morphologies that can be obtained when the solvent is eliminated from the demixed samples as well as the dependence of the thermal properties of cellulose tosylates on an additionally chemical modification is now under investigation and will be published elsewhere.
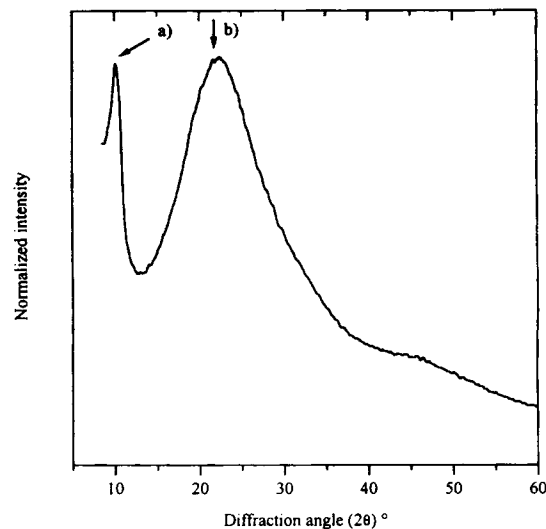

Figure 10   X-ray diffraction pattern of the system cellulose tosylate **20**/o-dichlorobenzene ($\phi_2 = 0.30$) in the dimixed state (room temperature): (a) diffraction maximum for the ordered structure; (b) amorphous signal.

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